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European Patent Office  
Office européen des brevets

⑪ Publication number:

0 155 070  
B1

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## EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: 29.03.89

⑯ Int. Cl. 4: C 03 C 25/02, G 02 B 6/22

⑰ Application number: 85300402.6

⑰ Date of filing: 22.01.85

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④ Coated optical fiber, fabrication process thereof and fabrication apparatus thereof.

③ Priority: 25.01.84 JP 10323/84  
29.05.84 JP 107502/84

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④ Date of publication of application:  
18.09.85 Bulletin 85/38

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⑤ Publication of the grant of the patent:  
29.03.89 Bulletin 89/13

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⑧ Designated Contracting States:  
DE FR GB

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Courier Press, Leamington Spa, England.

= VS 4801186

## Description

The present invention relates to a coated optical fiber prepared by coating an optical fiber with first and second layers, and the process as well as the apparatus for fabricating the same.

An optical fiber utilized for optical communication systems has a small outer diameter of generally 100  $\mu\text{m}$  order and is a very fragile material. Thus, if such optical fibers are used without any reinforcement, they rupture at a very lower strength than the original strength (about 7 kg) thereof, because of friction or generation of surface damages during the fabrication or cable-manufacturing process of these optical fibers. Namely, it is not possible to form a transmission line with a high reliability. In this connection, there is proposed a method for coating the surface of an optical fiber immediately after spinning thereof with a plastic material in order to protect the surface of the optical fiber and to maintain initial strength thereof.

Such plastic coating consists generally of a primary coating layer and a secondary layer. The primary coating layer is a buffer layer made of a material of a low Young's modulus and has purposes of maintaining initial strength of the optical fiber and to prevent increase in microbending loss of the fiber due to uneven secondary coating. On the other hand, the secondary coating layer is made of a thermoplastic resin having a higher Young's modulus than that of the primary coating layer and has purposes to easily handle optical fibers in cabling or the like process thereof.

Heretofore, there have been proposed the following two types of coated optical fibers. One of the two types is a coated optical fiber having a tight construction in which a primary coating layer made of a thermosetting resin such as silicone resin or the like adheres tightly to a secondary coating layer made of a thermoplastic resin such as nylon, polyamide resin or the like. Another type is a coated optical fiber of loose tube type having such a construction that a primary coating layer made of a thermosetting resin such as acrylic resins or the like is loosely held in a protective plastic tube (secondary coating layer) made of a thermoplastic resin such as polyethylene terephthalate, polypropylene or the like.

In either of the aforesaid tight and loose tube types of coated optical fibers, it is required that primary coating layer adheres to the surface of an optical fiber in order to protect the optical fiber. Either of thermosetting and thermoplastic resins is applicable to the coating of an optical fiber as described above. However, the materials which have heretofore been industrially employed are limited to thermosetting resins such as silicone, urethane-acrylate, epoxy-acrylate or the like resins. For the sake of coating an optical fiber with a thermosetting resin as described above, an optical fiber immediately after spinning is coated with such a resin by means of an applicator such as die or the like, and the resin thus coated is cured by heating or ultraviolet-ray irradiation.

However, such primary coating material of the thermosetting resin composition as described above and the coating method utilizing the coating material involve some problems from a viewpoint of economization of optical fiber cables. The reasons follows. The first disadvantage resides in that costs of the coating materials are expensive. For example, silicone resin which has been widely used as a primary coating material is more expensive by one figure than that of a thermoplastic resin which is generally used. The second problem resides in that when a spinning rate of optical fibers increases, slip arises between coating materials and the optical fibers. Besides, these coating materials require two processes of coating and curing. As a consequence, the optical fibers cannot be coated with such coating materials. In other words, use of these coating materials is limited to a range wherein a coating rate thereof is comparatively low (100 m/min or less in case of industrial fabrication). Furthermore, the third problem resides in that a transmission loss of the optical fiber coated with such type of materials as mentioned above increases at a low temperature of  $-60^\circ\text{C}$  or less, because of an increase of Young's modulus in a material for the primary coating layer in the vicinity of its crystallizing temperature of glass transition temperature.

On the other hand, in case that a nylon layer is used as a secondary coating layer, a transmission loss increases due to orientation relaxation or recrystallization of such nylon layer after the nylon layer is heated at a high temperature of  $+80^\circ\text{C}$  or more.

As primary coating materials other than those described above, thermoplastic resins such as ethylene-vinyl acetate copolymer (EVA) and the like have been proposed in combination with hot-melt method wherein a die for coating operation is heated to melt EVA. In this case, however, there are the same problems as those of the materials described above. Besides, the latter materials and such hot-melt method are not suitable for coating optical fibers of continuous length at a high speed, since heating temperature is limited by heat stability of the resin used.

As a method for coating a wire material with thermoplastic resin, use is generally made of an extrusion coating method in which an extruder is utilized in a technical field of coating metal wires such as those used for power line, communication line or the like. As a die-nipple construction of this case, there are two types, i.e., pressure type construction shown in Fig. 1 and tube type shown in Fig. 2.

More specifically, Figs. 1 and 2 are typical views each showing a construction of conventional die-nipple wherein reference numeral 1 designates a glass fiber, 2 concentrically disposed thermoplastic rubber composition and thermoplastic resin in molten state, 3 a die, 4 a nipple, 5 an inner diameter of the nipple 4, 6 a distance from the extreme end of the nipple 4 to an outlet of the die 3, 7 an inner diameter of the die 3, and 8 a nozzle length of the die 3.

The pressure type means a construction wherein a metal wire is coated with a thermoplastic resin inside a die. The pressure type has advantages in that a coating layer adhering to metal wires is obtained

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and that high-speed coating of the wire is realized by controlling the pressure of the resin used.

On the other hand, in the tube type, a metal wire is coated with a tube-shaped resin which has been extruded while applying drawdown. The advantages of the tube type resides in that a thickness of the coating film is easily controlled and the coating is performed at a high-speed coating while maintaining a comparatively low coating tension.

In these die-nipple constructions, however, glass fibers cannot directly be coated with a thermoplastic resin. A major reason resides in a difference between breaking characteristics of metal wires and glass fibers. More specifically, while breaking strength does not decrease in case of metal wire even if they are in contact with a solid material, breaking strength of glass fiber decreases easily in case that the glass fiber comes into contact with the inner surface of a nipple. Thus, in case of coating a glass fiber, it is necessary not only to make a clearance defined between a fiber and the inner surface of a nipple wider (usually, by several tens  $\mu\text{m}$ ) than that in case of coating a metal wire, but also to keep coating tension low as much as possible. As a result, coating tension increases due to the generation of excessive resin pressure, i.e., fiber breaking arises as well as a back flow of a resin occurs by means of the high pressure through the inside of the nipple in this die-nipple construction of pressure type. Accordingly, it is not possible to obtain a coating layer having a stable film thickness over continuous length thereof at a rate of several tens m or more per minute.

On one hand, in the tube type construction, it is difficult to obtain a coating layer adhering to a fiber. Besides, such fibers vibrate, since a tube-shaped molten resin thus extruded has no effect of maintaining the fiber (centering force), so that the fiber comes easily in contact with the inner surface of the nipple. for this reason, fiber strength decreases and in addition, the coating cannot be processed at a high speed.

As described above, there was a problem in economization for the fabrication of an optical fiber when a primary coating material of a thermosetting resin and the coating method which have heretofore been employed for the fabrication of a metal wire are used for the fabrication of an optical fiber. Furthermore, there was also such problem that a thermoplastic resin cannot be used for such primary coating material, since extrusion coating method which has been utilized for metal wire coating cannot be applied to the coating of a fiber.

On the other hand, concerning secondary coating layer, linear expansion coefficient of materials used for both tight and loose types are of the order of  $10^{-4}\text{C}^{-1}$  and such a value is far larger than that of fiber itself which is of the order of  $10^{-7}\text{C}^{-1}$ . For this reason, in case of a tight coating fiber, the fiber causes microbending because of expansion and contraction of the secondary coating layer due to temperature change so that there is an increase in loss due to the microbending. Furthermore, in such a coated fiber of the tight type, a comparatively long cooling step of about several meters is required in the step for secondary coating. Such cooling step is performed so that the orientation in fibers along the longitudinal direction thereof which occurs in extrusion coating step for secondary coating material is removed as much as possible by means of slow cooling. If such slow cooling is insufficient, relaxation of orientation proceeds even at ordinary temperatures so that a secondary coating layer contacts gradually. As a result, compressive strain is applied to fibers, and consequently microbending loss increases gradually. As the secondary coating step is speeded up, it becomes actually impossible to provide such a slow cooling step which can sufficiently correspond to such high-speed secondary coating step. In these circumstance, relaxation in orientation of such secondary coating layer causes a bottleneck so that a coating speed is limited to about several tens m/min. Thus, it has been a problem that the coating speed cannot be increased as described above.

As another tight type coating fiber, there has been proposed a coating fiber in which glass fibers are appended longitudinally to fiber yarn stock having a silicone buffer layer along the length thereof, and they are fixed by curing a thermosetting resin applied thereon to form a secondary coating layer. A linear expansion coefficient of the secondary coating layer of the fiber core wire is of the order of  $10^{-5}\text{C}^{-1}$  and therefore, increase in microbending loss is remarkably suppressed. In this case, however, such a low linear expansion coefficient of the secondary coating layer is due to linear expansion coefficient (in the order of  $10^{-7}\text{C}^{-1}$ ) of glass fiber, whilst the thermosetting resin itself has inevitably a high linear expansion coefficient (in the order of  $10^{-4}\text{C}^{-1}$ ). In addition, since thermosetting resin requires a comparatively long curing time, such a disadvantage that secondary coating speed is very slow still remains.

In a coated fiber of the loose tube type, loss due to macroscopic fiber bending caused by expansion and contraction of a protective plastic material forming a secondary coating layer is relaxed by affording suitably an extra length to the fiber in the loose tube. However, since a difference between linear expansion coefficients of the secondary coating layer and the fiber itself is significant, increase in microbending loss due to expansion and contraction of the secondary coating layer is still observed.

In order to prevent the increase in microbending loss due to a difference between linear expansion coefficients of the secondary coating layer and the fiber, there have been proposed a coated fiber prepared by stretching and orientating a loose tube along the longer direction thereof at its melting point or less under solid state in core wire manufacturing step. A linear expansion coefficient of the secondary coating layer of the coated fiber is  $10^{-6}\text{C}^{-1}$  or less and hence, increase in microbending loss is remarkably suppressed. There were, however, such disadvantages that a comparatively long heating oven is required for the stretching and orientation of loose tubes in order to fabricate a coated fiber of loose tube type which are stretched and orientated as described above, that its production line becomes long, because it is

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required to place a heat-treating oven after a stretching-heating oven in order to prevent heat shrinkage of the stretched loose tube at a high temperature, that for this reason, it is difficult to increase a manufacturing speed, and that precise control for manufacturing steps is necessary for controlling extra length of the fiber.

5 As mentioned above, a thermoplastic resin having a lower cost than that of thermosetting resins may be used as a secondary coating material, and the above-mentioned extrusion coating may be adopted for the coating method therefor. In this case, however, it is premised on the use of a thermosetting resin as its primary coating material, so that the primary and secondary coating steps become inevitably separated steps regardless of continuous or discontinuous steps. In view of the above, economization of optical fibers based on an increase of a coating speed is limited in the coating techniques at present.

10 As set forth above, there were such disadvantages in prior art that microbending loss based on a difference between linear expansion coefficients of a coating material and a fiber increases in both coating structures of tight and loose tube types, so long as secondary coating materials (thermoplastic resins) which are employed at present are utilized, and further that its coating speed is limited and besides 15 additional apparatus such as a heat-treating oven and the like is required, since the secondary coating layer is orientated in a coating method (extrusion coating) which is generally used at present on the basis of the former reason, so that loss due to its orientation relaxation increases.

15 The present invention seeks to eliminate the above described disadvantages involved with conventional-coated optical fibers and to provide a coated optical fiber which has excellent transmission characteristics at low and high temperatures and which is inexpensive.

20 The present invention also seeks to provide a process which can be carried out at high speed for fabricating an inexpensive coated optical fiber having excellent transmission characteristics at low and high temperatures.

25 The present invention further seeks to provide a highly reliable process for fabricating coated optical fibers wherein a wide range of thermoplastic resins can be used and a wide range of coating thicknesses can be obtained, the process also improving the workability of such coated optical fibers when they are connected together.

30 The present invention also seeks to provide an inexpensive and highly reliable apparatus for carrying out the latter process.

35 It is known from the Patent Abstracts of Japan Vol. 6, No. 113, Kokai No. 57-47748, to provide a coated optical fiber in which a first layer, which is a rubber composition, is disposed around the circumference of an optical fiber, and a second layer which is a thermoplastic resin composition, is disposed around the circumference of the first layer.

40 However, the present invention is characterized in that (a) the rubber composition of the first layer is a thermoplastic rubber composition which has a Young's modulus of 0.1 GPa or less and which is capable of extrusion coating, (b) the thermoplastic resin composition of the second layer exhibits liquid crystallizability in the molten state and its oriented state is maintained by forcible cooling immediately after the coating step, and (c) the thermoplastic resin composition has a linear expansion coefficient of 7 × 10⁻⁵°C⁻¹ or less and a Young's modulus of 4.3 GPa or more and is capable of extrusion coating.

45 The thermoplastic rubber composition of the first layer may contain a styrene copolymer or an olefine copolymer. The thermoplastic rubber composition of the first layer may comprise a styrene/butadiene block copolymer containing 20–40% by weight of styrene, a naphthenic processing oil and a heat stabilizer as the major components. Each amount of the naphthenic processed oil and the heat stabilizer can be 5–150 parts by weight and 0.5–5 parts by weight, respectively, with respect to 100 parts by weight of the styrene/butadiene block copolymer. The thermoplastic resin composition of the second layer may be composed of polyethylene terephthalate-p-hydroxybenzoic acid copolymer containing 40–70 mol% of p-hydroxybenzoic acid or a blend prepared from the copolymer and other polymer, and the resin composition may present molecular orientation in lengthwise direction of the fiber at a rate of shear of  $10^2 \text{ sec}^{-1}$  or more.

50 The thermoplastic rubber composition of the first layer may contain an ethylene- $\alpha$ -olefine copolymer. Where the thermoplastic rubber composition of the first layer comprises:

- A: a styrene/butadiene block copolymer (20–40 wt% styrene concentration),
- B: a naphthenic processing oil, and
- C: a heat stabilizer,

55 as the major components, the concentrations of the respective components of the composition can be so determined that

$$\frac{B}{A + B} = 5-40 \text{ wt\%} \text{ and } \frac{B}{A + B + C} \geq 2 \text{ wt\%}.$$

60 The thermoplastic resin composition of the second layer may be selected from the group consisting of all aromatic polyesters, aromatic-fatty polyesters, all aromatic polyester amides, aromatic-aliphatic polyester amides, aromatic polyazomethines, aromatic polyester-carbonates, the mixtures thereof, or mixtures of the high-molecular materials with the other high-molecular materials.

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It is known from the Patent Abstracts of Japan Vol. 6, No. 31, Kokai No. 56-149353 to provide a process wherein an optical fiber is simultaneously coated with different thermoplastic resin layers and is cooled after coating. However, the coating method, the coating materials and the purpose of cooling are different to those used in the invention.

5 The invention provides a process which is characterized in that the optical fiber is simultaneously extrusion-coated with (a) a first layer of a thermoplastic rubber composition which has a Young's modulus of 0.1 GPa or less and which is capable of extrusion coating, and (b) a second layer of a molecular-orientated thermoplastic resin composition which exhibits liquid crystallizability in molten state and which has a linear expansion coefficient of  $7 \times 10^{-6} \text{C}^{-1}$  or less which has a Young's modulus of 4.3 GPa or more and which is capable of extrusion coating. In such a process the optical fiber is extrusion-coated, by an applicator, immediately after the spinning step end, where the coated optical fiber travels at a speed of  $V(\text{m/sec})$ , at least the second layer is forcibly cooled to the crystallization temperature of the molecular-orientated thermoplastic resin composition or less before the coated optical fiber reaches a distance  $x$ , from the outlet of the applicator, which satisfies the condition  $x/V \leq 1$ .

10 15 The coated optical fiber may be cooled forcibly by use of coolant, which is selected from the group consisting of liquids, gases, or the mixtures thereof having a specific heat of 0.1 kcal/kg°C or more at an ordinary temperature and a thermal conductivity of 0.01 kcal/m.hr.°C or more. The molecular-orientated thermoplastic resin composition may be a thermotropic liquid crystalline high-molecular material. The molecular-orientated thermoplastic resin composition may be selected from polyethylene terephthalate-p-

20 hydroxybenzoic acid copolymers containing 40-70 mol% of p-hydroxybenzoic acid or blends prepared from the copolymers and other polymers, and the resin composition may exhibit molecular orientation, in lengthwise direction of the fiber at a rate of shear of  $10^2 \text{ sec}^{-1}$  or more. The thermoplastic rubber composition may contain a styrene copolymer or an ethylene- $\alpha$ -olefine copolymer. The thermoplastic rubber composition may comprise a styrene/butadiene block copolymer containing 20-40% by weight of styrene, a naphthenic processing oil, and a heat stabilizer as the major components, and an amount of the naphthenic processing oil may be 5-150 parts by weight with respect to 100 parts by weight of the styrene/butadiene block copolymer.

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30 The present invention also provides apparatus for fabricating the latter-mentioned coated optical fiber and which is characterized in that the apparatus comprises an extruding machine for extruding the thermoplastic rubber composition and the molecular-orientated thermoplastic resin composition, a crosshead for simultaneously coating the optical fiber with the extruded thermoplastic rubber composition and the molecular-orientated thermoplastic resin composition to form the first and second layer around the optical fiber, and first cooling means disposed on the outlet side of the crosshead for forcibly cooling the coated optical fiber at a liquid crystal temperature of the liquid crystalline thermoplastic resin composition of the second layer or less. The first cooling means has a length  $x(\text{m})$  which satisfies the condition  $x/V \leq 1$  for a fiber travelling at a speed of  $V(\text{m/sec})$ . The crosshead also has at least a nipple and die, an extreme and portion of the nipple, which is located inside said nozzle forming a straight pipe having an inner diameter which is larger than the diameter of the optical fiber and less than 0.5 mm.

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40 In such apparatus, the interior of the cooling means may be filled with coolant which is brought into contact with the coated optical fiber to cool the coated optical fiber. The apparatus may further comprise second means for cooling the coolant which is to be introduced into the interior of the first cooling means; and means for circulating the coolant between the first cooling means and the second cooling means.

45 Embodiment of the invention will now be described in more detail with reference to some of the accompanying drawings in which:

50 Figs. 1 and 2 are schematic views each showing the construction of a conventional die-nipple for coating a metal wire;

Fig. 3 is a graph illustrating the relationship between the concentration of styrene and Young's modulus in SBS;

55 Fig. 4 is a graph illustrating the relationship between melt viscosity and the rate of shear in case of an SBS/processed oil composition at 260°C;

Fig. 5 is a graph illustrating the relationship between the coefficient of linear expansion and the rate of shear at 240°C in case of PET/POB (40 mol% of PET);

Fig. 6A is a graph illustrating the relationship between the coefficient of linear expansion  $\alpha$  of PET/POB extruded at a rate of shear of  $10^3 \text{ sec}^{-1}$  at an extrusion temperature of 240°C and concentration of POB;

Fig. 6B is a graph illustrating the relationship between Young's modulus  $E$  of PET/POB extruded at a rate of shear of  $10^3 \text{ sec}^{-1}$  at an extrusion temperature of 240°C and the concentration of POB;

Fig. 7 and 8 are sectional views each showing schematically an embodiment of a crosshead used in an apparatus for fabricating a coated optical fiber according to the present invention;

Fig. 9 is a sectional view showing an embodiment of a specific construction of such a crosshead;

Fig. 10 is a perspective view showing the disassembled crosshead shown in Fig. 9;

Fig. 11 and 12 are schematic typical views each showing an embodiment of an apparatus for fabricating a coated optical fiber in the second mode of the present invention;

Fig. 13 is a graph illustrating a loss spectrum of the coated optical fiber according to the present invention;

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Fig. 14 is a characteristic diagram wherein loss is plotted with respect to  $\lambda^{-4}$  in the case of the coated optical fiber of Fig. 13;

Fig. 15 is a characteristic diagram illustrating comparatively temperature-dependency of transmission loss in case of a coated optical fiber according to the present invention and a conventional coated optical fiber; and

Fig. 16 is a characteristic diagram illustrating comparatively shrinkage strain of a coated layer according to the present invention and a conventional coated layer, both after eliminating the optical fiber from the coated optical fiber, during cooling after heat-treatment.

The present invention was achieved as a result of a research of novel coating materials which may 10 replace conventional liquid thermoplastic resins. The present inventors have studied thermoplastic resins and elastomers being suitably applicable for an extrusion coating method by which high speed coating is possible and found that a resin composition comprising a styrene/butadiene/styrene block copolymer (hereinafter referred to simple as "SBS"), a processed oil, and a heat stabilizer as major components thereof was most suitable for a first coating layer.

15 Various thermoplastic rubbers such as styrene elastomers, polyolefine elastomers, urethane elastomers, polyester elastomers, polybutadiene elastomers, nylon elastomers, the compositions obtained therefrom and the like are applicable for coating materials of the first layer of a coated optical fiber according to the present invention. Among others, particularly preferable are styrene elastomers, polyolefin elastomers, and the compositions thereof.

20 Styrene elastomers include styrene/ethylene-butylne/styrene block copolymer (SEBS), styrene/butadiene/styrene block copolymer (SBS), styrene/isoprene/styrene block copolymer (SIS) and the like. Among others, the most preferable is SBS.

25 More specifically, SBS has a lower Young's modulus and a lower glass transition temperature than those of the other thermoplastic resins and elastomers and besides SBS has properties required for coating materials in view of transmission loss. Processed oil reduces significantly melt viscosity of a resin composition prepared by adding the processed oil to resin so that such resin composition is effective for the speeding up of a coating speed for an optical fiber. As well known, since SBS involves double bonds, it crosslinks and gels easily at a high temperature. In this respect, heat stabilizer is effective for preventing such crosslinkage and gelation as well as increase in Young's modulus with time due to the crosslinkage.

30 A concentration of 40—95% by weight is suitable for SBS which is a major component of the resin composition according to the present invention, whilst a concentration of 5—60% by weight is suitable for processed oil which is another major component of the resin composition. While there is such an advantage in that a coat itself formed is highly reliable in the case where a concentration of SBS is high, there is such a disadvantage in that the coating speed is limited because of its high melt viscosity. On the contrary, when a concentration of SBS is low and hence a concentration of processed oil is high, there is such an advantage that its coating speed may be increased because a melt viscosity of resin composition becomes low, but there is such a disadvantage that reliability of the coat itself formed is impaired. Furthermore, processed oil has such advantages that it decreases not only melt viscosity of a resin composition, but also Young's modulus thereof.

40 Although a concentration of heat stabilizer is not specifically limited, such heat stabilizer is generally used within a range of 0.05—5%.

45 A thermoplastic elastomer called generally SBS may be classified roughly into two categories, i.e., linear and radial types, and both of them are applicable for the present invention. While SBS of such linear type includes various structures such as  $S_1B_2S_2$ ,  $B_1S_1B_2S_2$  and the like (wherein  $S_1$  and  $S_2$  indicate styrene blocks, and  $B_1$  and  $B_2$  indicate butadiene blocks), a structure and a manufacturing process of SBS per se used in the present invention are not particularly limited. Namely, a ratio of styrene block and butadiene block may arbitrarily be changed in such SBS.

50 A range of SBS which may be contained in a resin composition used for the optical fiber coating material of the present invention will be described hereinbelow. Fig. 3 is a graph illustrating a relationship between a concentration of styrene (weight %) in SBS (abscissa) and Young's modulus (GPa) thereof (ordinate). From Fig. 3, it is understood that conditions of 0.1 GPa or less of Young's modulus are satisfied by such composition having 40% by weight or less styrene concentration. However, as a styrene concentration is decreased, heat stability of SBS deteriorates so that coating of fibers becomes impossible. While such an advantage that Young's modulus of SBS reduces is obtained in the case where a 55 concentration of styrene is reduced, there is such a disadvantage that coating properties deteriorate because flowability of such resin composition decreases. Conversely, although the flowability becomes favorable in the case where a concentration of styrene becomes high, Young's modulus becomes also high so that it is not preferable from the viewpoint of transmission loss of coated optical fibers.

60 It is a requisite for a resin composition used for the first layer of the present invention that a Young's modulus thereof is 0.1 GPa or less at ordinary temperature as mentioned above. Such optical fibers coated with a resin composition Young's modulus of which exceeds 0.1 GPa increase easily transmission loss.

65 It is required that a gelation time at coating temperature is 30 seconds or more as a standard for heat stability under which fibers can be coated. Since such a resin composition having less than 30 seconds gelation time exhibits poor heat stability, there is such a case where crosslinkage appears, Young's modulus of the resin composition increases and transmission loss of a coated optical fiber increases, and

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there is also such an outstanding case where gelation is observed at the time of coating an optical fiber so that no coating is formed.

It was found that such composition satisfying such conditions that a gelation time of SBS containing 2% by weight of Irganox 1010 (Manufactured by Ciba Geigy S.A.) as a heat stabilizer is 30 seconds or more at 260°C which is selected as a usual coating temperature was limited to a composition having a styrene concentration of 20% by weight or more. For this reason, a concentration of styrene contained in SBS is limited to a range of 20—40 weight %.

Furthermore, it is preferable that a rubber composition utilized in the present invention has a melt viscosity of  $10^5$  poise or less at the time of coating the rubber composition.

In general, a coating temperature ranges 150—260°C. When a melt viscosity exceeds  $10^5$  poise, flowability of such resin composition becomes inferior even at a coating temperature within the aforesaid temperature range. As a result, the coating speed is limited.

Fig. 4 is a graphical representation illustrating a relationship between a melt viscosity (ordinate) and a rate of shear (abscissa) in respect of SBS having 28 weight% styrene concentration, with a parameter of a concentration of naphthenic processed oil (wt. %) (the numbers appeared in Fig. 4) at 260°C. From Fig. 4, it is understood that compositions involving 5% by weight or more processed oil satisfies the above-described conditions. On the other hand, with an increase in concentration of such processed oil, resistance to blocking of SBS decreases. According to the research conducted by the present inventors, it was found that such an SBS composition containing processed oil of 60% by weight or more became sol, and 20 exhibited flowability even at an ordinary temperature.

A rubber composition layer exhibiting flowability at ordinary temperature cannot hold optical fibers therein, but merely functions as an interposed layer. In other words, when an external force is applied to the rubber composition layer, there are portions in which an optical fiber comes in direct contact with its second layer, so that such composition cannot be used as a coating material for the first layer according to 25 the present invention.

Examples of the processed oil which can be used in the present invention include paraffinic processed oils, aromatic processed oils, naphthenic processed oils and the like. Among others, particularly preferable is a naphthenic processed oil compatible with the butadiene block in SBS. The naphthenic processed oils to be utilized in the present invention are not specifically limited by specific gravity, viscosity, pour point, 30 aniline point,  $C_A$ ,  $C_N$ ,  $C_P$  and the like.

Heat stabilizers employed in this invention are those generally referred to as antioxidants, aging inhibitors or the like. While types of such heat stabilizer are not particularly limited in the present invention, compounds as enumerated hereinbelow may generally be used singly or in combination with two or more of them. Examples of such compounds include zinc dibutyl thiocarbamate (ZDBC), tetrakis - [methylene - 35 3 - (3',5' - di - tert - butyl - 4' - hydroxyphenyl)propionate]methane, phenothiazine, phenyl -  $\alpha$  - naphthylamine, phenyl -  $\beta$  - naphthylamine, p - isopropoxydiphenylamine, N,N' - diphenyl - p - phenylenediamine, N - isopropyl - N' - phenyl - p - phenylenediamine, 2,6 - di - tert - butyl - 4 - methylphenol, 4 - hydroxymethyl-2,6 - di - tert - butylphenol, 2,6 - di - tert - butyl -  $\alpha$  - dimethylamino - p - cresol, 2,2' - methylene - bis - (4 - methyl - 6 - tert - butylphenol), 4,4' - thiobis - (6 - tert - 40 butyl - 3 - methylphenol) and 1,3,5 - trimethyl - 2,4,6 - tris(3,5 - di - tert - butyl - 4 - hydroxybenzyl)benzene.

The resin composition according to the present invention comprises SBS, a processed oil and a heat stabilizer as the major components, and optionally thermoplastic resin, thermoplastic elastomer, liquid oligomer, silane coupling agent or the like can be added to the resin.

Additives optionally used in the present invention may include styrene elastomers such as styrene/isoprene block copolymers (SIS), styrene/ethylene-butylene/styrene block copolymers (SEBS) and the like, olefine elastomers, urethane elastomers, polyester elastomers, 1,2-polybutadiene elastomers, polyethylene, polystyrene, petroleum resin or synthetic rubbers such as 1,4-polybutadiene, styrene-butadiene rubber (SBR) and the like, antiozonant, ultraviolet absorber, plasticizer, softener, lubricant and 50 the like.

Furthermore, polyolefine elastomers utilized in the present invention may include copolymers of  $\alpha$ -olefines such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, allylcyclopentane, allylcyclohexane, allylbenzene, 3-methyl-1-butene, 3-cyclohexyl-1-butene, 3-phenyl-1-butene, 4-phenyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 5-phenyl-1-pentene, 3-methyl-1-hexene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 5-methyl-1-hexene, 3,5,5-trimethyl-1-hexene, 5-methyl-1-heptene, 6-methyl-1-heptene, 4,6,6-trimethyl-1-heptene, vinylcyclopropane, vinylcyclopentane, vinylcyclohexane, 2-vinylbicyclo(2,2,1)heptane and the like as well as copolymers of ethylene and the aforesaid  $\alpha$ -olefines. Among others, particularly preferable are copolymers obtained from ethylene and the aforesaid  $\alpha$ -olefines, and more preferable 60 materials are copolymers prepared from ethylene and an  $\alpha$ -olefine selected from the group consisting of propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-dodecene and 1-octadecene. These copolymers have low Young's modulus at a low temperature and also excellent formability.

In the present invention, a ratio of copolymerization for olefine elastomers is not specifically defined. Such olefine elastomers may be used alone. The olefine elastomers may also be used in the form of rubber compositions which contain optionally various processed oils and various additives such as plasticizer,

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antioxidant, adhesion imparting agent, aging inhibitor and the like as in the case of SBS.

Molecular-orientated thermoplastic resins to be used for a second layer coating material may be high molecular materials (thermotropic liquid crystalline high molecular materials) exhibiting liquid crystalline state in molten condition. Examples of the high molecular materials may include all aromatic polyesters,

5 aromatic-aliphatic polyesters, all aromatic polyester amides, aromatic-aliphatic polyester amides, aromatic polyazomethines, aromatic polyester carbonates, mixtures of the aforesaid high molecular materials, or mixtures of the aforesaid high molecular materials and the other high molecular materials, or reaction products obtained from the aforesaid high molecular materials and chain extenders and the like.

The all aromatic polyesters may include (1) copolymers prepared from one or more of aromatic dicarboxylic acids and one or more of aromatic diols via condensation thereof, (2) copolymers prepared by condensing one or more of aromatic hydroxycarboxylic acids, and (3) copolymers prepared from one or more of aromatic dicarboxylic acids and one or more of aromatic diols as well as one or more of aromatic hydroxycarboxylic acids through condensation thereof.

The aromatic-aliphatic polyesters may include (1) copolymers obtained from one or more of aromatic dicarboxylic acids and one or more of aliphatic diols and alicyclic diols via condensation thereof, (2) copolymers prepared from one or more of alicyclic dicarboxylic acids and one or more of aromatic diols through condensation thereof, and (3) copolymers prepared from one or more of aromatic hydroxycarboxylic acids and the dicarboxylic acid and diol in (1) or (2) through condensation thereof.

The all aromatic polyester amides may include (1) copolymers obtained from one or more of aromatic hydroxyamines and one or more of aromatic dicarboxylic acids via condensation thereof, (2) copolymers prepared from one or more of aromatic hydroxyamines, aromatic diamines, one or more of aromatic dicarboxylic acids, and one or more of the aromatic diols through condensation thereof, and (3) copolymers produced from one or more of aromatic hydroxycarboxylic acids, one or more of aromatic hydroxyamines, aromatic diamines, one or more of aromatic dicarboxylic acids, and one or more of aromatic diols by means of condensation thereof.

The aromatic-aliphatic polyamides may include (1) copolymers prepared from one or more of aromatic hydroxyamines, aromatic diamines, one or more of aromatic dicarboxylic acids, and one or more of aliphatic diols by means of condensation thereof, and (2) copolymers produced from one or more of aromatic hydroxyamines, aromatic diamines, one or more of alicyclic dicarboxylic acids, and one or more of aromatic diols, aliphatic diols via condensation thereof.

The aromatic polyazomethines may include copolymers produced from one or more of aromatic dialdehydes and one or more of aromatic diamines through condensation thereof.

The aromatic polyester-carbonates may include (1) copolymer prepared by polymerizing one or more of aromatic diols, one or more of aromatic dicarboxylic acids, and phosgene ( $\text{COCl}_2$ ), and (2) copolymers produced by polymerizing one or more of aromatic hydroxycarboxylic acids, one or more of aromatic diols, one or more of aromatic dicarboxylic acids and phosgene ( $\text{COCl}_2$ ).

In this connection, specific examples of the aromatic dicarboxylic acids may include such aromatic dicarboxylic acids as terephthalic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-triphenyl-dicarboxylic acid, 2,6-naphthalenedicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, diphenoxymethane-4,4'-dicarboxylic acid, diphenoxylbutane-4,4'-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, diphenylsulfide-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, diphenylketone-4,4'-dicarboxylic acid, diphenyldimethylmethane-4,4'-dicarboxylic acid isophthalic acid, 1,5-naphthalenedicarboxylic acid, and 1,4-naphthalenedicarboxylic acid as well as alkyl-, alkoxy-, aryl- or halogen-substituents or the aforesaid aromatic dicarboxylic acids such as chloroterephthalic acid, dichloroterephthalic acid, bromoterephthalic acid, methylterephthalic acid, dimethylterephthalic acid, ethylterephthalic acid, phenylterephthalic acid, and methoxyterephthalic acid.

Examples of the aromatic diols may include such aromatic diols as hydroquinone, resorcine, 4,4'-diphenyl diol, 4,4'-triphenyl diol, 2,6-naphthalene diol, diphenyl ether-4,4'-diol, diphenoxymethane-4,4'-diol, diphenylsulfide-4,4'-diol, diphenylsulfone-4,4'-diol, diphenylketone-4,4'-diol, diphenyl dimethylmethane-4,4'-diol, 1,5-naphthalene diol and 1,4-naphthalene diol as well as alkyl-, aryl-, alkoxy- or halogen-substituents of the aforesaid aromatic diols such as chlorohydroquinone, methylhydroquinone, phenylhydroquinone, t-butylhydroquinone, methoxyhydroquinone, 4-chlororesorcine, 4-methylresorcine and the like.

The aromatic hydroxycarboxylic acids may include such aromatic hydroxycarboxylic acids as p-hydroxybenzoic acid, m-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 5-hydroxy-1-naphthoic acid, 4-hydroxy-1-naphthoic acid, 6-hydroxy-1-naphthoic acid and the like as well as alkyl-, aryl-, alkoxy- or halogen-substituents of the aforesaid aromatic hydroxycarboxylic acids such as 3-methyl-4-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, 3-phenyl-4-hydroxybenzoic acid, 3-methoxy-4-hydroxybenzoic acid and the like.

60 The aliphatic diols may include linear or branched aliphatic diols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,5-pentanediol, 1,6-hexanediol and the like.

The alicyclic diols may include such alicyclic diols as trans-1,4-cyclohexane diol, cis-1,4-cyclohexane diol, trans-1,4-cyclohexane dimethanol, cis-1,4-cyclohexane dimethanol and trans-1,3-cyclohexane diol as well as alkyl, alkoxy- or halogen-substituents of the aforesaid alicyclic diols such as trans-1,4-(1-methyl)cyclohexanediol, trans-1,4-(1-chloro) cyclohexanediol and trans-1,4-(1-methoxy) cyclohexanediol.

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The alicyclic dicarboxylic acids may include such alicyclic dicarboxylic acids as trans-1,4-cyclohexane-dicarboxylic acid, cis-1,4-cyclohexanedicarboxylic acid, trans-1,3-cyclohexanedicarboxylic acid and the like as well as alkyl-, alkoxy- or halogen-substituents of the aforesaid alicyclic dicarboxylic acids such as trans-1,4-(1-methyl)cyclohexanedicarboxylic acid, trans-1,4-(1-chloro)-cyclohexanedicarboxylic acid and the like.

5 The aromatic hydroxyamines may include such aromatic hydroxyamines as p-hydroxyaniline, m-hydroxyaniline, 6-hydroxy-2-aminonaphthalene, 5-hydroxy-1-aminonaphthalene, 4-hydroxy-1-amino-naphthalene, 6-hydroxy-1-aminonaphthalene and the like as well as alkyl-, aryl-, alkoxy- or halogen-substituents of the aforesaid aromatic hydroxyamines such as 3-methyl-4-hydroxyaniline, 3-chloro-4-hydroxyaniline and the like.

10 The aromatic diamines may include such aromatic diamines as p-aminoaniline, m-aminoaniline, 2,6-diaminonaphthalene, 1,5-diaminonaphthalene, 1,4-diaminonaphthalene, 1,6-diaminonaphthalene and the like as well as alkyl-, aryl-, alkoxy- or halogen-substituents of the aforesaid aromatic diamines such as 3-methyl-4-aminoaniline, 3-chloro-4-aminoaniline, 3-phenyl-4-aminoaniline and the like.

15 The aromatic dialdehydes may include such aromatic dialdehydes as terephthalaldehyde, isophthalaldehyde, 2,6-naphthoaldehyde, 1,5-naphthoaldehyde, 1,4-naphthoaldehyde, 1,6-naphthoaldehyde and the like as well as alkyl-, aryl-, alkoxy- or halogen-substituents of the aforesaid aromatic dialdehydes such as 3-methylterephthalaldehyde, 3-chloroterephthalaldehyde, 3-phenylterephthalaldehyde and the like.

20 Furthermore, the other high molecular materials to be used in blends with the above described thermotropic liquid crystals may include engineering resins such as polyethylene terephthalate, polybutylene terephthalate, polycarbonate, polyarylate, polyether sulfone, polysulfone, polyphenylene sulfide, polyether and the like, or thermoplastic elastomers such as polyether ester, SBS and the like.

25 In addition, chain extenders to be utilized for reaction with the aforesaid thermotropic liquid crystals may include 1,4-phenylene-bis- $\Delta^2$ -oxazoline-2, 1,3-phenyl-bis- $\Delta^2$ -oxazoline-2, 1,2-phenylene-bis- $\Delta^2$ -oxazoline-2, 1,4-phenylene-bis(5-methyl- $\Delta^2$ -oxazoline-2), 1,3-phenylene-bis(5-methyl- $\Delta^2$ -oxazoline-2), 1,2-phenylene-bis-(5-methyl- $\Delta^2$ -oxazoline-2), 1,3-phenylene-bis(4-methyl- $\Delta^2$ -oxazoline-2), 1,4-phenylene-bis(4-methyl- $\Delta^2$ -oxazoline-2), 1,2-phenylene-bis(4-methyl- $\Delta^2$ -oxazoline-2), 1,2-phenylene-bis(4-ethyl- $\Delta^2$ -oxazoline-2), 1,2-ethylene-bis- $\Delta^2$ -oxazoline-2, 1,4-butylene-bis- $\Delta^2$ -oxazoline-2, 1,2,4-phenylene-tris- $\Delta^2$ -oxazoline-2 and the like.

30 A range of a composition applicable for a coating material of the second layer in the present invention will be described hereinbelow by taking a copolymer (PET/POB) prepared from polyethylene terephthalate (hereinafter referred to simply as "PET") and p-hydroxybenzoic acid (hereinafter referred to simply as "POB") as an example.

35 The term "thermotropic liquid crystal" herein used means crystalline polymer exhibiting anisotropy of crystal together with fluidity of liquid before the polymer becomes liquid by heating to melt the polymer. A polymer to which no external force is applied so that it is in liquid crystalline state is generally an aggregate of domains which are in a certain arranged order. It is known that such domains deform and flow, and hence disintegrate so that high molecular chains orientate along the direction of flow, when mechanical 40 external force is applied to such a system. As described above, since liquid crystal orientates along the direction of flow thereof, it is known that a melt viscosity of thermotropic liquid crystal is remarkably low, and further that the higher a rate of shear, the lower a melt viscosity under shearing flow. PET/POB copolymer in non-orientated state has a linear expansion coefficient of the order of  $10^{-5} \text{C}^{-1}$  and a Young's modulus of several GPa and hence, such copolymer itself does not have low linear expansion coefficient and high Young's modulus. However, such PET/POB copolymer being in orientated state exhibits low linear expansion coefficient and high Young's modulus along its orientated direction.

45 As a method for flowing and orientating thermotropic liquid crystal, there is a method for injecting the liquid crystal from a small nozzle. In other words, it is possible in injection or extrusion molding that high molecular chains are orientated in injecting or extruding direction by injecting such thermotropic liquid crystal from a small die. Since the liquid crystal thus orientated maintains its orientated state even after temperature drops, such liquid crystal exhibits low linear expansion coefficient and high Young's modulus along the direction of orientation.

50 In a preferred example of the present invention, a PET/POB copolymer under orientated state is used for the second coating layer on the basis of the fact that the PET/POB copolymer exhibits low linear expansion coefficient and high Young's modulus along the orientated direction. Degree of orientation of PET/POB copolymer depends remarkably upon a rate of shear at the time of extruding the copolymer.

55 Fig. 5 is a graphical representation illustrating a relationship between a rate of shear ( $\text{sec}^{-1}$ ) (abscissa) and a coefficient of linear expansion ( $10^{-5} \text{C}^{-1}$ ) along the extrusion direction (ordinate) in the case when a PET/POB copolymer (PET content being 40 mol%) is extruded from a nozzle by utilizing a capillary viscometer at 240°C. As is apparent from Fig. 5, it is understood that orientation is improved with the increase in a rate of shear, so that a coefficient of linear expansion becomes low. In case that a rate of shear is  $10^2 \text{ sec}^{-1}$  or more, a coefficient of linear expansion becomes  $1 \times 10^{-5} \text{C}$  or less. From the above results, it is found that such a PET/POB copolymer which has been orientated at a rate of shear of substantially  $10^2 \text{ sec}^{-1}$  or more is suitable for the second coating layer in the present invention. Further, in this case, it was observed that Young's modulus along the orientated direction was such a high value of 10 GPa or more.

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Ease of orientation or crystallizability of PET/POB copolymer depends significantly upon an amount of POB contained. Fig. 6A is a graphical representation illustrating a relationship of a coefficient of linear expansion ( $10^{-6} \text{C}^{-1}$ ) (ordinate) of a PET/POB copolymer extruded at a shear rate of  $10^3 \text{ sec}^{-1}$  at  $240^\circ\text{C}$  with an amount of POB (mol%) abscissa. Fig. 6B is a graphical representation illustrating a relationship of a

5 Young's modulus (GPa) (ordinate) of the PET/POB copolymer with an amount of POB (mol %) (abscissa). From the results, it is found that liquid crystallizability appears with the increase of POB mol% and hence the copolymer orientates easily, so that the linear expansion coefficient thereof decreases. It is also found that a coefficient of linear expansion becomes  $10^{-6} \text{C}^{-1}$  or less when an amount of POB is about 40 mol%. As a result, it is found that an amount of POB is preferably 40 mol% or more in a PET/POB copolymer to be used for the second coating material.

10 With the increase of POB mol% in PET/POB copolymer, its linear expansion coefficient becomes low along the direction of orientation and the Young's modulus thereof becomes high, whilst there appears a disadvantage that elongation in the direction of orientation decreases remarkably so that the coated layer of such copolymer is easily broken down by bending the same. In this connection, the second coated layer of a fiber (coating outer diameter was 1 mm) coated with a PET/POB (=30/70) copolymer as the first coated layer (coating outer layer was 0.4 mm) was broken down at a bending radius of 5 mm.

15 As a result of detailed research of a relationship between POB content and allowable (breaking) bending radius, it was found that such allowable bending radius further increases with the increase of POB content. When easiness or the like for handling coated optical fibers is taken into consideration, it is required that an allowable bending radius is 5 mm or less. Thus, the upper limit of POB content in a PET/POB copolymer for the second coating layer according to the present invention is 70 mol%.

20 It is also possible to utilize blends of PET/POB copolymer and other polymers as the second coating materials. In this case, non-crystalline polycarbonate or thermoplastic polyether ester, or rubber compositions comprising these components as their major components can be effectively used as blend polymer, and it is preferable that a POB content in a blend prepared after blending the PET/POB copolymer with another polymer is within a range of 40—70 mol%.

25 Thermoplastic rubber compositions, particularly styrene elastomer compositions used in the present invention are soluble in organic solvents such as benzene, toluene and the like at an ordinary temperature. Thus, there is no fear of producing surface defects on optical fibers in stripping operation (i.e., removal of coated layer) necessary for connecting optical fibers to each other by using the above-described organic solvent. Accordingly, there is such an advantage that an optical fiber of the present invention is excellent in connecting workability, and connecting portions of the optical fibers have high strength.

30 For the sake of concurrently coating an optical fiber with a first layer of a thermoplastic rubber composition and a second layer of a thermoplastic resin in the present invention, these materials are supplied to a crosshead by means of separate feeding apparatuses such as extruding machines or gear pumps. The crosshead has a die-nipple construction wherein an extreme end portion of the nipple forms a straight pipe having an inner diameter of 0.5 mm or less and the extreme end of the straight pipe locates inside a die nozzle.

35 Fig. 7 is a sectional view showing schematically an embodiment of a die-nipple construction of the crosshead for simultaneously coating two layers according to the present invention.

40 The apparatus for fabricating a coated optical fiber in accordance with the present invention has been made on the basis of results of detailed research in respect of relationships of coating film thickness, unevenness and a strength of coated fibers with a construction of a crosshead, particularly a construction of a die-nipple.

45 A fundamental outline of an embodiment of a die-nipple construction of the present invention will be described in conjunction with Fig. 7.

50 In Fig. 7, reference numeral 11 designates a nipple through which an optical fiber 1 passes, and the extreme end portion 11A of which forms a straight pipe having an inner diameter  $d$  of 0.5 mm or less. A die 12 having an inner diameter  $D$  is placed with a predetermined distance with respect to the nipple 11. A supply passage 13 is formed concentrically along the circumference of the nipple 11, so that a thermoplastic rubber composition for forming a first layer is supplied through the passage 13. A supply passage 14 is also concentrically formed along the circumference of the die 12, so that a thermoplastic resin for forming a second layer is supplied through the passage 14. The rubber composition 15 and the resin 16 being in molten state after passing through both the supply passages 13 and 14 form two layers in a gap 17 defined between the nipple 11 and the die 12 as shown in Fig. 7 and they are delivered from the extreme end portion 11A of the nipple 11 to the outlet of the die 12. In Fig. 7,  $L_1$  designates a distance from the extreme end portion 11A of the nipple 11 to the outlet of the die 12 and  $L_2$  designates a nozzle length of the die 12.

55 In the gap 17 defined between the nipple 11 and the die 12, both the molten materials are accelerated up to a predetermined speed by means of an extruding machine while keeping two-layered condition thereof. In this case, although there is produced a resin pressure corresponding to its flow velocity generated in inlet portion of a nozzle 12A of the die 12, this resin pressure decreases because of viscous flow of the resin in the gap 17 between the nipple 11 and the die 12, so that the pressure is extremely low at the extreme end portion 11A of the nipple 11. Hence a tension applied to the fiber 1 reduces significantly as compared with that of the above-mentioned pressure type die-nipple construction. Besides, there is an

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extremely low possibility that the nipple 11. Furthermore, the molten materials 15 and 16 flow adhesively together with the fiber 1 within a region of distance  $L_1$  extending from the extreme end portion 11A of the nipple 11 to the outlet of the nozzle 12A of the die 12. For this reason, first and second coating layers 18 and 19 being adherent to the fiber 1 can be obtained unlike the case of the above-mentioned tube type die-nipple construction. In addition, a viscous flow derived from the molten rubber composition 15 and resin 16 functions to maintain the fiber 1 at the center of the die nozzle 12A so that there is such an advantage that the possibility of eccentricity of the fiber 1 becomes very low and hence, such risk that the fiber 1 comes into contact with the inner surface 11C of the nipple 11 can also be prevented.

Fig. 8 illustrates another embodiment of the crosshead in an apparatus for fabricating a coated optical fiber according to the present invention. The crosshead has the same construction as that shown in Fig. 7 except that the inner diameter of the die 12 is formed in two stages, i.e., the inner diameter  $D_1$  of a die nozzle portion 12B corresponding to the extreme end portion 11A of the nipple 11 is made larger whilst the inner diameter  $D_2$  of a die nozzle portion 12C positioned on the downstream side from the extreme end portion 11A of the nipple 11 is made smaller than the inner diameter  $D_1$ .

Fig. 9 shows a specific embodiment of the aforementioned condition of the crosshead, and Fig. 10 shows the disassembled condition of the crosshead shown in Fig. 9 together with extruding machines for the first and second layers.

In Figs. 9 and 10, reference numeral 21 designates a crosshead cover, the inside of which has a tapered opening 23 for inserting a cartridge 22 and a hole 24 communicating with the opening 23 for supplying rubber composition to the opening 23. The crosshead cover 21 is connected to the extruding machine 100 for extruding a thermoplastic rubber for forming the first layer, so that thermoplastic rubber is supplied from the extruding machine 100 to the cartridge 22 through the supply hole 24.

The cartridge 22 is of substantially truncated conical shape, the interior of which has a stepped opening 26 being capable of receiving a nipple holder 32. Around the circumference of the cartridge 22, a recess 27 is formed to form a passage of the thermoplastic rubber in a gap between the cartridge 22 and the crosshead cover 21 is defined, when the cartridge 22 is inserted into the crosshead cover 21. The cartridge 22 is radially provided with a plurality of apertures 28 communicating with the opening 26 around the whole circumference thereof on the substantially downstream side of the recess 27. Though a depth of the recess 27 varies dependent upon positions, the thermoplastic rubber is supplied with circumferentially uniform pressure to the interior of the opening 26 through the radial apertures 28. The bottom of the cartridge 22 is provided with a base 29, on which a supply hole 30 for introducing a thermoplastic resin such as a liquid crystalline high-molecular material into the opening 26 of the cartridge 22 from the extruding machine 101 is defined.

The cartridge 22 is inserted into the opening 23 from the underside of the crosshead cover 21, and a screw positioned on the outside at the upper part of the cartridge 22 which is projected from the upper part of the crosshead cover 21 is secured by means of a nut 31, so that the cartridge 22 is fixed to the crosshead cover 21.

A nipple holder 32 is mounted on the upper part of the cartridge opening 26. The nipple holder 32 is provided with a hole 35 for holding a nipple 33 and at the same time inserting a guide screw 34 thereinto.

The guide screw 34 is provided with a nozzle 36 having an inner diameter of several mm which functions as a guide in the case that the fiber 1 is introduced into the nipple 33 at the time of commencing wire drawing of the fiber 1. This nozzle 36 is based on the consideration for workability and therefore, such means is not essentially required during operation of an apparatus. A portion of the screw 37 is screwed into an opening 38 defined inside the upper part of the cartridge 22.

The nipple holder 32 holds the nipple 33 and at the same time, ensures a flow path for coating materials. More specifically, the upper outside tapered portion of the nipple holder 32 is inserted from the underside of the cartridge opening 26 thereinto to fit it with the cartridge opening 26. The first layer coating material flowed into the interior through the cartridge opening 26 passes through the gap defined between the nipple holder 32 and the cartridge 22 and is introduced into a die 39 disposed inside the lower part of the cartridge opening 26. The extreme end of the nipple holder 32 is tapered in parallel with the tapered plane of the die 39 so as to define a flow path of a constant distance therebetween.

An exposed base of the nipple 33 is placed in face to face relation with respect to the circumference of a tapered nozzle at the extreme end of the nipple holder 32. An extreme end portion 40 of the nipple 33 forms a straight pipe, which is inserted into a nozzle 41 formed inside the die 39. The die 39 is provided with the nozzle 41 having a tapered portion for forming flow paths for the first and second layer coating materials. These coating materials are forcibly delivered through the nozzle 41 along the traveling direction of the fiber 1. The nipple holder 32 and the tapered surface of the nipple 33 are in contact with the first layer coating material, whilst the tapered surface of the die 39 is in contact with the second layer coating material.

A distributor 42 is secured to the circumference of the die 39. The distributor 42 holds the die 39 inside thereof. The distributor 42 is provided with a groove 43 for supplying the second layer coating material with circumferentially uniform pressure on the circumference thereof. The groove 43 is successively branched from the position corresponding to the supply hole 30 and extends upwardly. The upper surface of the distributor 42 is in face to face relation with the tapered upper surface of the die 39, so that the second layer

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coating material introduced through the groove 43 is further introduced into the tapered nozzle 41 of the die 39.

5 The distributor 42 containing the die 39 inserted therein is inserted from the underside of the cartridge opening 26 thereinto, so that the flow of the second layer coating material is turned back by means of a portion of an inner flange 44 formed inside the cartridge opening 26 so that the second layer coating material joins with the first layer coating material in the gap between the nipple holder 32 and the die 39 to be introduced in the die 39 as two-layered flow.

10 A cap nut 45 holds the distributor 42 and which is screwed with a screw 46 formed on the outer lower surface of the cartridge 22. In this case, since a pitch of screw thread of the screw 46 is known already, the spacing defined between the nipple 33 and the die 39 is precisely established by rotating the cap nut 45 from the screwed position with a suitable number of rotations in such a way that the nipple 33 or the nipple holder 32 comes in contact with the die 39.

15 It is to be noted that the upper structure of the crosshead, i.e., a resin flow path structure extending from the outlet of the extruding machine to the die-nipple arrangement is not specifically limited to the above described embodiment. Any structure may be applied to the present invention so far as each of thermoplastic resin materials is concentrically placed in a spacing defined between the die and the nipple, and these materials may be uniformly supplied without unevenness and stagnation thereof.

20 According to the extrusion coating in the present invention, not only the simultaneous coating of the two layers, but also single layer coating is possible. In either case, a rate of shear in the die nozzle becomes maximum on the wall surface of the nozzle. For instance, when a fiber (125  $\mu\text{m}$  diameter) is coated by using a nozzle having an inner diameter of 0.9 mm, a rate of shear on the wall surface of the nozzle becomes  $10^3 \text{ sec}^{-1}$  or more, when a fiber speed is 10  $\text{m/min}$  or less. Namely, a coefficient of linear expansion of the second coated layer becomes  $1 \times 10^{-6} \text{ C}^{-1}$  or less under normal coating conditions in accordance with the present invention, so that no particular operation is required in this connection. Furthermore, since linear expansion coefficient or Young's modulus of the orientated second coated layer are maintained even after cooling the same, apparatuses such as heat-treating oven or the like used in conventional secondary coating methods become unnecessary. As a result, a fiber drawing apparatus can be simplified and coating can be performed at a high speed. In addition, two layers can be coated in a single coating step.

25 As will be described in the following Comparative Example 3, a back flow of resin through the inside of the nipple is observed in case that an inner diameter of the straight pipe portion of the nipple is 0.5 mm or more.

30 Accordingly, in this case, a fiber of continuous length cannot be coated. Thus, an inner diameter of the nipple is limited to a range of less than 0.5 mm.

35

### EXAMPLE GROUP I

While the present invention will be described in more detail hereinbelow in fiber of conjunction with examples and comparative examples, it is to be understood that the present invention is not limited to such examples.

40

In the following examples and comparative examples, the following materials were used:

fiber diameter: 125  $\mu\text{m}$

fiber speed: 300  $\text{m/min}$

outer diameter of first (inner) layer: 400  $\mu\text{m}$

outer diameter of second (outer) layer: 900  $\mu\text{m}$

composition of first (inner) layer coating material: 98% by weight of SBS/oil blend comprising 70% by

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weight of a styrene-butadiene-styrene copolymer (28 weight% styrene concentration) and 30% by weight of a naphthenic oil, and 2% by weight of heat stabilizer second (outer) layer coating material: PET/POB copolymer (including 40 mol% PET).

#### Example 1

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Coating experiment was effected by employing the die-nipple having the construction shown in Fig. 7 wherein the dimensions were: 0.4 mm inner diameter of the nipple, 0.9 mm inner diameter of the die, 7 mm die nozzle length, and 2 mm distance from the extreme end of the nipple to the outlet of the die nozzle. In this case, resin pressure became 320  $\text{kg/cm}^2$ , and the fiber could be coated over a length of 18 km or more. An eccentricity (a distance between the centers of the fiber and the coating) was  $\pm 15 \mu\text{m}$  or less. Average 55 breaking strength of the coated fiber (gauge length: 10 m, n = 50) was 6.7 kg per one fiber. A transmission loss of the coated optical fiber was 2.8 dB/km at a wavelength of 0.85  $\mu\text{m}$  and 0.6 dB/km at a wavelength of 1.55  $\mu\text{m}$ . The values of the aforesaid transmission loss did not vary within a temperature range from -75°C to +80°C.

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#### Comparative Example 1

The die-nipple having the construction shown in Fig. 1 was utilized and the dimensions were: 0.18 mm inner diameter of the nipple, 0.45 mm die nozzle diameter, and 5 mm die nozzle length. In this case, resin pressure exceeded 400  $\text{kg/cm}^2$  and the resin held fiber in a region where a flow rate of the resin was comparatively slow in the vicinity of the inlet of the die nozzle, so that no coating could be carried out.

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### Comparative Example 2

The die-nipple having the construction shown in Fig. 2 was used and the dimensions were: 2 mm nipple inner diameter, 4.5 mm die nozzle diameter, and 8 mm die nozzle length. In this case, resin pressure became 260 kg/cm<sup>2</sup>, and the fiber could be coated over a length of 8 km. However, since the surface of the fiber was not adherent to the first (inner) layer, an eccentricity ranged from  $\pm 80$  to 250  $\mu\text{m}$ , and an average breaking strength was 2.0 kg per one fiber (gauge length 10 m; n = 50). A transmission loss of the coated optical fiber was 3.0 dB/km at a wavelength of 0.85  $\mu\text{m}$  and 0.8 dB/km at a wavelength of 1.55  $\mu\text{m}$ . The values of the aforesaid transmission loss did not vary within a temperature range from -75°C to +80°C.

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### Example 2

The die-nipple having the construction shown in Fig. 8 was utilized and the dimensions were: 0.4 mm inner diameter of the nipple, die nozzle diameter of 1.5 mm at the inlet portion and 0.9 mm at the outlet portion, and 2.5 mm distance from the extreme end of the nipple to the outlet of the die nozzle. In this case, resin pressure became 380 kg/cm<sup>2</sup>, and the fiber could be coated over a length of 7 km or more. An average breaking strength of the coated optical fibers was 6.4 kg per one fiber, and a transmission loss thereof was substantially the same as that of Example 1.

### Comparative Example 3

In Example 1, a nipple having an inner diameter of 0.5 mm was utilized. In this case, resin pressure, eccentricity, breaking strength, transmission loss and the like were the same as those of Example 1, but a back flow of the resin arose through the inside of the nipple, so that the fiber was broken at the time that the fiber was coated over a length of 2 km.

As described above, a coated optical fiber having two-layer coated structure composed of a first (inner) layer of a thermoplastic rubber composition having a low Young's modulus and a second (outer) layer of a thermoplastic resin having a low linear expansion coefficient and a high Young's modulus is fabricated in a single and high speed coating process in accordance with the present invention and hence there is an advantage in that significant economization of optical fiber cables becomes possible.

Next, the second aspect of the present invention will be described hereinbelow.

According to the detailed research by the present inventors, it has been found that a coated optical fiber fabricated by forcibly cooling at least the second layer of the coated layers at the melting point thereof or less within one second immediately after the coating exhibits excellent transmission characteristics, particularly excellent low-temperature characteristics over a wide range of coating film thickness and a wide coating speed.

With the above in view, in the second aspect of the present invention, a coated optical fiber is fabricated by simultaneously coating the first layer of a thermoplastic rubber composition and the second layer of a thermoplastic resin composition of molecular orientation on an optical fiber immediately after spinning the optical fiber by heating to soften the optical fiber preform with the use of a crosshead of one extruding machine. At least the second layer of the simultaneously coated two layers in the crosshead is forcibly cooled at crystallization temperature or less of the thermoplastic resin composition of molecular orientation.

In the apparatus for fabricating a coated optical fiber according to the present invention, a cooling cylinder for cooling the coating of the coated optical fiber is provided on the outlet side of the crosshead of the extruding machine with or without contacting the crosshead. The interior of the cylinder is filled with liquid, gas, or the mixture thereof to bring it into contact with the coated optical fiber.

The present invention has been made on the basis of the results of detailed studies of relationships between film thicknesses of first layer (low Young's modulus layer) and second layer (high Young's modulus and low linear expansion coefficient layer) and transmission characteristics of the resulting coated optical fibers as well as relationships between coating speed and transmission characteristics of the coated optical fibers.

Namely, as is understood from the following examples of the present invention and comparative examples, a transmission loss at a low temperature increases with the increase in ratio of a film thickness between the first and second layers as well as a coating speed in the case where no treatment is given for the coated optical fiber after the coating thereof (i.e., air-cooling), whilst no increase in such a transmission loss as described above is observed in the case where the coated fiber is cooled forcibly immediately after the coating thereof by the use of liquid and/or gas coolant. Although the reasons for the above phenomena are not clear, it may be presumed that microbending of the glass fiber arises easily due to contraction based on orientation relaxation of the second layer in the case of air-cooling (slow cooling), whilst molecular orientation of the second layer is instantly fixed in case of fast cooling and as a result, there is no contraction, so that microbending of the glass fiber is prevented.

Fig. 11 is a schematic view showing an embodiment of a construction of an apparatus according to the present invention. In Fig. 11, reference numeral 51 designates a fiber preform, 52 a heating oven, 53 a diameter monitor for an optical fiber 54, 55 a crosshead of an extruding machine having the construction as described above, 56 and 57 first and second layer extruding machines, 58 a cooling cylinder for a coated optical fiber 59 supplied from the crosshead 55, 60 a fiber take-up capstan, 61 a cooling and/or supply tank for coolant, 62 a pump for circulating the coolant, 63 a three-way cock, 64 an outlet for the cooling cylinder,

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and 65 a diameter monitor for the coated optical fiber 59, respectively. The coated optical fiber 59 is prepared by forming the first and second layers 66 and 67 around the optical fiber 54.

5 In the crosshead 55 of the extruding machine, the optical fiber 59 having the two layers simultaneously coated is cooled by the cooling cylinder 58 filled with the coolant. The coolant is either circulated through the cooling tank 61 at a constant temperature, or supplemented from the cooling-supply tank 61 under a low temperature condition. In the case where the coolant is gas, the three-way cock 63 is opened. In the case where the coolant is liquid, the outlet 64 of the cooling cylinder 58 is of a sealed construction in order to prevent leakage of the liquid, or cooling liquid leaked from the cooling cylinder outlet 64 is circulated to the cooling cylinder 58 by the pump 62.

10 In conventional extrusion coating for metal wire materials, coated layers are annealed or slowly cooled in order to promote orientation relaxation of the coated layers. On the contrary, in the present invention, the second layer is cooled rapidly immediately after the coating in order to prevent orientation relaxation of the second layer. Such cooling is carried out within one second after coating the second layer at the crystallization temperature thereof or less. Thus, it is required to cool the second layer at the crystallization temperature thereof or less before the coated optical fiber reaches a distance satisfying a condition expressed by  $x/V \leq 1$ , where  $V$  (m/sec.) is a traveling speed of the fiber, and  $x$  (m) is a distance from the crosshead outlet to the outlet of the cooling cylinder 58. In other words, the upper limit of the length of the cooling cylinder 58 is the distance  $x$  and in this case, the inlet of the cooling cylinder 58 is in contact with a die of the crosshead 55.

15 20 In the case where the coolant is liquid, the apparatus may be modified as shown in Fig. 12. Here, a pulley 68 is provided inside the cooling cylinder 58 in order to prevent the leakage of the liquid, and the coated fiber is taken out from the upper part of the cooling cylinder 58 through a pulley 69, as shown in Fig. 12. In this case, it is preferable that the distance  $x$  from the outlet of the crosshead 55 to the pulley 68 is within the range as mentioned above.

25 30 35 A coolant for a coated optical fiber used in the present invention may be liquid, gas, or the mixture thereof having a specific heat of 0.1 kcal/kg.°C or more at an ordinary temperature and a thermal conductivity of 0.01 kcal/m.hr°C or more. Examples of such coolant include water, glycerin, alcohols such as methyl alcohol, ethyl alcohol and the like, various oils such as mineral oil, processed oil and the like, and inert gases such as Freon, helium, neon and the like. The coolant comes into contact with the coated optical fiber 59 in the cooling cylinder 58 positioned immediately below the extruding machines 56 and 57 to forcibly cool the coated optical fiber 59. Here, a temperature and a flow rate for supplying the coolant are set so as to satisfy the aforesaid condition  $x/V \leq 1$ .

40 45 50 The second aspect of the present invention will be described more specifically in connection with the following examples of the present invention and comparative examples. This aspect of the present invention is not limited thereto.

### EXAMPLE GROUP II

Coated optical fibers were fabricated in accordance with the conditions shown in Table 1, wherein a diameter of glass fiber used was 125  $\mu$ m, SBS means a composition comprising 70 parts by weight of SBS (28 weight% styrene concentration), 30 parts by weight of naphthenic oil, and 2 parts by weight of a stabilizer, and SEBS means a composition comprising SEBS (14 weight% styrene concentration) in place of SBS (its make-up is the same as that of the SBS composition). PET/POB (40/60 mole%) copolymer (310°C melting point, 170°C crystallization temperature) was used for a second layer coating material. Furthermore, an extrusion temperature of the crosshead 55 of the extruding machine utilized was 270°C. A die nozzle diameter was 0.9 mm. A die nozzle length, was 5 mm. A nipple inner diameter was 0.2 mm and a land length (a distance from the extreme end portion 11A of the nipple 11 to the outlet of the die nozzle 12A in Fig. 7 or 8) were 2 mm. In addition, a cooling length for the coated optical fiber 59 in the lower part of the extruding machine crosshead 55 was 1.5 m, and a distance between the cooling cylinder 58 and the outlet of the crosshead 55 was 10 cm, so that a relationship between fiber speed  $V = 100$  cm/min and distance  $x$  m from the crosshead outlet to the cooling cylinder outlet became  $x/V = 1.6/100$  min.  $\approx 1$  sec. In these examples, coolant was supplied at an ordinary temperature.

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Table 1 (Example Group II)

Reference	First Layer Material	Outer Diameter of 1st Layer (μm)	Outer Diameter of 2nd Layer (μm)	Coating Speed (m/min)	Coolant	Temperature <sup>3)</sup> (°C)	Transmission <sup>1)</sup> Loss (dB/km)	
							20°C	-75°C <sup>2)</sup>
Example 1	SBS	500	-	100	-	200	2.4	+0
	SBS	500	-	500	-	230	2.5	+0
	SEBS	900	-	100	-	220	2.5	+0.1
	SEBS	900	-	500	-	250	2.5	+0.2
Example 1	SBS	500	600	100	Water	70	2.4	+0
	SBS	500	1000	100	Water	90	2.5	+0
	SBS	500	1000	500	Water	110	2.6	+0
	SEBS	500	600	100	Glycerin	90	2.5	+0.1
Comparative Example 1	SEBS	500	1000	100	Glycerin	110	2.4	+0.2
	SEBS	500	1000	500	Glycerin	130	2.4	+0.2
	SBS	500	1000	500	Helium	160	2.6	+0.3
	SEBS	500	1000	500	Helium	160	2.8	+0.4
Comparative Example 1	SBS	500	600	100	-	210	2.8	+0.4
	SBS	500	1000	100	-	230	4.5	+10.5
	SBS	500	1000	500	-	260	6.3	+32.0
	SEBS	500	600	100	-	200	2.7	+0.8
Comparative Example 1	SEBS	500	1000	100	-	240	5.7	+14.5
	SEBS	500	1000	500	-	250	8.5	+42.0
	SBS	300	1000	500	-	260	9.4	+45.0
	SBS	7	-	-	-	-	-	-

1) Measured at a wavelength of 0.85 μm

2) Amount in change from a value of loss at 20°C

3) Surface temperature of the coated layer at the point (outlet of cooling cylinder) apart from crosshead outlet by 1.6 m

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### EXAMPLE GROUP III

Coated optical fibers were fabricated in accordance with the conditions shown in Table 2 wherein the coating conditions in Table 2 are the same as those of Table 1.

5 Giving an outline of Tables 1 and 2, while favorable transmission characteristics can be obtained in such fibers coated with the single layer of SBS or SEBS (Reference Examples 1—4 in Table 1) without cooling forcibly them, the transmission characteristics were remarkably deteriorated in case that the two layers were simultaneous coated, if its coating material composition was out of the preferred range or if the coated fiber was not forcibly cooled, and particularly in case that its coated film thickness was thick and the coating speed was high (Comparative Examples 1—7 in Table 1, and Comparative Examples 1—4 in Table 2).  
10 2. On the contrary, it is apparent, according to the present invention, that good transmission characteristics are obtained, even if a coated film thickness is thick and a coating speed is high (Examples 1—8 in Table 1, and Examples 10—12 in Table 2).

### EXAMPLE GROUP IV

15 Coated optical fibers were fabricated in accordance with the conditions shown in Table 3—1 and 3—2, and the results thereof are also shown in Tables 3—1 and 3—2.

As is apparent from Tables 3—1 and 3—2, it is understood that when a composition of coating material and a rate of shear were out of the preferred range, mechanical properties of the resulting coated optical fibers were deteriorated.

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POLYESTER/STYRENE/TEREPHTHALATE / POLYDADYBENZOC<sub>6</sub>HE<sub>11</sub>

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Table 2 (Example Group III)

	First Layer 1)			Second Layer 3)			Coating Speed (m/min)	Coating (20°C/km) (dB/km)	Transmission Loss (20°C/5°C) (dB/km)
	Composition <sup>2)</sup> (SBS/Oil, Part by weight)	Coated Outer Diameter (μm)	Composition <sup>3)</sup> (PET/POB - molar)	Coated Outer Diameter (μm)	Coolant				
Example	1) 6)	95/5	200	40/60	400	none	300	2.4	+0.2
	2) 7)	95/5	200	40/60	400	none	300	2.6	+0.2
	3) 6)	40/60	300	40/60	500	none	300	2.7	+0.1
	4) 7)	70/30	300	40/60	500	none	300	2.5	+0.2
	5) 6)	95/5	200	40/60	400	none	600	2.4	+0.2
	6) 8)	70/30	300	60/40	400	none	300	2.5	+0.3
	7) 8)	70/30	300	30/70	400	none	300	2.7	+0.3
	8) 8)	70/30	300	50/50	400	none	300	2.6	+0.2
	9) 8)	70/30	300	40/60 <sup>9)</sup>	400	none	300	2.3	+0.2
	10) 8)	70/30	300	40/60	1000	water	300	2.4	+0.1
	11) 8)	70/30	300	40/60	1000	water	600	2.6	+0.1
	12) 8)	70/30	400	40/60	1200	water	600	2.5	+0.2
Comparative Example	1) 6)	100/0	200	40/60	400	none	—	(Fiber Broken) (Impossible to extrude 1st Layer)	
	2) 6)	30/70	200	40/60	400	none	—	(Fiber Broken) (Impossible to extrude 1st Layer)	
	3) 8)	70/30	300	70/30	500	water	300	2.8	+8.6
	4) 8)	70/30	300	20/80	500	water	300	2.7	+7.8

- 1) Styrene thermoplastic rubber (SBS) compositions
- 2) Containing 2 parts by weight of a heat stabilizer (Irganox 1010)
- 3) PET/POB and the compositions thereof
- 4) Measured at wavelength 0.85 μm
- 5) Amount in change from a value of loss at 20°C
- 6) 40 wt% styrene concentration
- 7) 20 wt% styrene concentration
- 8) 24 wt% styrene concentration
- 9) Containing 30% by weight of polyester elastomer (Hytrel)

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Table 3-1. (Example Group IV)

	Composition (PET/POB, mol%)	Rate of Shear (sec <sup>-1</sup> )	Extrusion Temperature (°C)	Linear Expansion Coefficient (°C <sup>-1</sup> ) 25°C	Young's Modulus (GPa) 25°C	Allowable Bending Radius (mm)
Example 1	60/40	1x10 <sup>3</sup>	240	1-2x10 <sup>-5</sup>		
Comparative Example 1	70/30	1x10 <sup>3</sup>	240	6.1x10 <sup>-5</sup>		
Example 2	30/70	1x10 <sup>3</sup>	240	-3.5x10 <sup>-6</sup>		
Comparative Example 2	20/80	1x10 <sup>3</sup>	240	-4.0x10 <sup>-6</sup>		
Example 3	40/60	1x10 <sup>2</sup>	240	7x10 <sup>-6</sup>	4.3	
Example 4	50/50	1.4x10 <sup>2</sup>	220	7x10 <sup>-5</sup>	10	
Example 5	50/50	9.8x10 <sup>2</sup>	220	4x10 <sup>-6</sup>	21	
Comparative Example 3	40/60	2x10 <sup>1</sup>	240	1.8x10 <sup>-5</sup>	3	
Example 6	40/60	1.9x10 <sup>2</sup>	310	-2.5x10 <sup>-6</sup>	18.2	
Example 7	50/50	1.9x10 <sup>2</sup>	315	1x10 <sup>-6</sup>	11.4	
Example 8	40/60+30 wt%	1.9x10 <sup>2</sup>	220	-2x10 <sup>-6</sup>	18	
Example 9	40/60+30 Hytrel	1.9x10 <sup>2</sup>	300	-1x10 <sup>-6</sup>	11	

Table 3-2 (Example Group IV)

Example	Composition (PET/POB, mol%)	Rate of Shear (sec <sup>-1</sup> )	Extrusion Temperature (°C)	Linear Expansion Coefficient (°C <sup>-1</sup> ) 25°C	Young's Modulus (GPa) 25°C	Permissible Bending Radius (mm)
10	NA/POB= 50/50	210	300	-4x10 <sup>-6</sup>	40.0	(ε <sub>b</sub> -3%)
11	NA/POB= 40/60	210	300	-6x10 <sup>-6</sup>	47.3	
12	PET/POB/TPA/ IPA/BiSA=					
	45/45/2.5/2.5/5	170	280	9x10 <sup>-6</sup>	12.1	(ε <sub>b</sub> -5%)
	+2wt% Chain Extender					
13	PET/POB=55/45 +2wt% Chain Extender	230	280	1.0x10 <sup>-5</sup>	7.5	(ε <sub>b</sub> -6.6%)
14	TPA/POB/NA/BP =15/65/10/10	210	275	-4x10 <sup>-6</sup>	50.4	(ε <sub>b</sub> -3.6%)
15	PET/POB=48/52	210	325	1.1x10 <sup>-5</sup>	8.8	(ε <sub>b</sub> -5.9%)

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As described above, in accordance with the second aspect of the present invention, an optical fiber is coated with the first layer of a thermoplastic rubber composition having a low Young's modulus and the second layer of thermoplastic resin of molecular orientation with wide ranges of a coating film thickness and a coating speed and hence, there is an advantage that inexpensive and highly reliable coated optical fibers are obtained. In addition, the coated layer of the coated optical fiber can chemically be dissolved to remove it without damage of surface of the optical fibers at the time of connecting them to one another, so that there are such advantages that workability of the coated optical fiber of the present invention is excellent and that the strength in connected portions of the optical fibers is also improved.

Transmission characteristics of the coated optical fiber according to the present invention will be discussed hereunder.

Loss spectrum of a coated optical fiber having two coating layers accordance with SBS/PET-POB coated by simultaneous extrusion (a coating speed of 100 m/min, and a diameter of first layer/a diameter of second layer = 500/600  $\mu\text{m}$ ) is illustrated in Fig. 13, whilst a relationship between loss and  $1/\lambda^4$  ( $\lambda$ : wavelength) is shown in Fig. 14. In Fig. 13, loss peaks in the vicinities of  $\lambda = 0.95, 1.25$  and  $1.4 \mu\text{m}$  are caused by OH absorption due to the use of a VAD preform which has not yet been dehydrated. Loss values of the coated optical fiber was  $2.42 \text{ dB/km}$  at  $\lambda = 0.85 \mu\text{m}$  and  $1.50 \text{ dB/km}$  at  $\lambda = 1.30 \mu\text{m}$ . The minimum loss was  $0.61 \text{ dB/km}$  ( $\lambda = 1.59 \mu\text{m}$ ). As is clear from Fig. 14, a loss due to incomplete structure (a value obtained by extrapolating  $\lambda^{-4}$  to 0) is hardly observed. These characteristics were substantially the same as those of a conventional optical fiber coated with silicone.

Fig. 15 shows temperature dependency of a transmission loss ( $0.85 \mu\text{m}$  wavelength) with respect to a temperature change of  $+20^\circ\text{C} \rightarrow -75^\circ\text{C} \rightarrow +80^\circ\text{C} \rightarrow +20^\circ\text{C}$ . A loss increases rapidly at  $-40^\circ\text{C}$  or less (first cycle) in a conventional optical fiber (marked  $\Delta$ ) coated with silicone/nylon, whilst a loss hardly increases up to  $-75^\circ\text{C}$  and its value was  $+0.05 \text{ dB/km}$  or less in the optical fiber coated simultaneously with two layers of SBS/PET-POB (marked  $O$ ). This is because  $T_g$  ( $-70^\circ\text{C}$  or less) of SBS composition for the first layer is lower than that ( $-40$  to  $-60^\circ\text{C}$ ) of silicone. Furthermore, a starting temperature of increase in loss rises ( $0^\circ\text{C}$  or less, second cycle) by means of thermal hysteresis at  $+80^\circ\text{C}$  in the conventional silicone/nylon coated optical fiber, whilst no such increase in loss was observed in the coated optical fiber having two layers simultaneously coated according to the present invention.

Fig. 16 shows shrinkage strain of nylon and PET-POB during the cooling to room temperature after heat treatment of the materials. In Fig. 16 shrinkage arises by heating nylon at  $80^\circ\text{C}$  for several minutes, whilst no shrinkage was observed in PET-POB even at a higher temperature ( $170^\circ\text{C}$ ). From these results, it is understood that the increase of loss in the second cycle of Fig. 15 is promoted by the shrinkage strain due to thermal hysteresis of the nylon layer, while the loss does not increase even by thermal hysteresis of  $80^\circ\text{C}$  or more in the coated optical fiber having two layers coated simultaneously with SBS/PET-POB according to the present invention.

### Claims

1. A coated optical fiber comprising an optical fiber, a first layer which is a rubber composition and which is disposed around the circumference of said optical fiber, and a second layer which is a thermoplastic resin composition and which is disposed around the circumference of said first layer, characterized in that (a) said rubber composition of said first layer is a thermoplastic rubber composition which has a Young's modulus of  $0.1 \text{ GPa}$  or less and is capable of extrusion coating, (b) said thermoplastic resin composition of said second layer exhibits liquid crystallizability in molten state and its oriented state is maintained by forcible cooling immediately after the coating step and (c) said thermoplastic resin composition has a linear expansion coefficient of  $7 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  or less and a Young's modulus of  $4.3 \text{ GPa}$  or more and is capable of extrusion coating.

2. A coated optical fiber as claimed in claim 1, characterized in that the thermoplastic rubber composition of said first layer contains a styrene copolymer or an olefine copolymer.

3. A coated optical fiber as claimed in claim 1, characterized in that the thermoplastic resin composition of said second layer is composed of polyethylene terephthalate-p-hydroxybenzoic acid copolymer containing 40—70 mol% of p-hydroxybenzoic acid or a blend prepared from said copolymer and other polymer, and that said resin composition presents molecular orientation in lengthwise direction of the fiber at a rate of shear of  $10^2 \text{ sec}^{-1}$  or more.

4. A coated optical fiber as claimed in claim 1 characterized in that the thermoplastic rubber composition of said first layer comprises:

A: a styrene/butadiene block copolymer (20—40 wt% styrene concentration),

B: a naphthenic processing oil, and

C: a heat stabilizer,

as the major components, and that concentrations of the respective components of said composition are so determined that

$$\frac{B}{A + B} = 5-40 \text{ and } \frac{B}{A + B + C} \geq 2 \text{ wt\%}.$$

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5. A coated optical fiber as claimed in claim 1, characterized in that said thermoplastic resin composition of said second layer is selected from the group consisting of all aromatic polyesters, aromatic-fatty polyesters, all aromatic polyester amides, aromatic-aliphatic polyester amides, aromatic polyazomethines, aromatic polyester-carbonates, the mixtures thereof, or mixtures of said high-molecular materials with the other high-molecular materials.

6. A process for fabricating a coated optical fiber in which an optical fiber preform is spun by heating so that said optical fiber preform is softened to form an optical fiber, characterized in that said optical fiber is extrusion-coated simultaneously with (a) a first layer of a thermoplastic rubber composition which has a Young's modulus of 0.1 GPa or less and which is capable of extrusion coating and (b) a second layer of a molecular-orientated thermoplastic resin composition which exhibits liquid crystallizability in molten state and which has a linear expansion coefficient of  $7 \times 10^{-5} \text{C}^{-1}$  or less which has a Young's modulus of 4.3 GPa or more and which is capable of extrusion coating; said extrusion-coating being carried out immediately after the spinning step by an applicator and that at least said second layer, of said simultaneously coated first and second layers, is forcibly cooled to the crystallization temperature of the molecular-orientated thermoplastic resin composition or less before the coated optical fiber reaches a distance  $x$  from the outlet of the applicator, where  $x/V \leq 1$  and  $V(\text{m/sec})$  is the speed of travel of the optical fiber.

7. A process for fabricating a coated optical fiber as claimed in claim 6, characterized in that said coated optical fiber is cooled forcibly by the use of coolant, which is selected from the group consisting of liquids, gases, or the mixtures thereof having a specific heat of 0.1 kcal/kg°C or more at an ordinary temperature and a thermal conductivity of 0.01 kcal/m.hr.°C or more.

8. A process for fabricating a coated optical fiber as claimed in claim 6, characterized in that said molecular-orientated thermoplastic resin composition is a thermotropic liquid crystalline high-molecular material.

9. A process for fabricating a coated optical fiber as claimed in claim 6, characterized in that said molecular-orientated thermoplastic resin composition is selected from polyethylene terephthalate-p-hydroxybenzoic acid copolymers containing 40—70 mol% of p-hydroxybenzoic acid or blends prepared from said copolymers and other polymers, and that said resin composition exhibits molecular orientation, in lengthwise direction of the fiber at a rate of shear of  $10^2 \text{ sec}^{-1}$  or more.

10. A process for fabricating a coated optical fiber as claimed in claim 6, characterized in that said thermoplastic rubber composition contains a styrene copolymer or an ethylene- $\alpha$ -olefine copolymer.

11. A process for fabricating a coated optical fiber as claimed in claim 6, characterized in that said thermoplastic rubber composition comprises a styrene/butadiene block copolymer containing 20—40% by weight of styrene, a naphthenic processing oil, and a heat stabilizer as the major components, and that an amount of said naphthenic processing oil is 5—150 parts by weight with respect to 100 parts by weight of said styrene/butadiene block copolymer.

12. An apparatus for fabricating a coated optical fiber wherein, immediately after spinning an optical fiber from an optical fiber preform by heating to soften said optical fiber preform, said optical fiber is coated with a first layer of a thermoplastic rubber composition which has a Young's modulus of 0.1 GPa or less and is capable of extrusion coating and a second layer of a molecular-orientated thermoplastic resin composition which exhibits liquid crystallizability in molten state and which has a linear expansion coefficient of  $7 \times 10^{-5} \text{C}^{-1}$  or less and a Young's modulus of 4.3 GPa or more and is capable of extrusion coating, characterized in that said apparatus comprises an extruding machine for extruding said thermoplastic rubber composition and said molecular-orientated thermoplastic resin composition, a crosshead for simultaneously coating said optical fiber with the extruded thermoplastic rubber composition and molecular-orientated thermoplastic resin composition to form said first and said second layer around said optical fiber, and first cooling means, having a length  $x(m)$  which satisfies the condition  $x/V \leq 1$  for a fiber travelling at a speed of  $V(\text{m/sec})$ , disposed on the outlet side of said crosshead for forcibly cooling the coated optical fiber at a liquid crystal transition temperature of the liquid crystalline thermoplastic resin composition of the second layer or less, and that said crosshead has at least a set of nipple and die, and an extreme end portion of said nipple, which is located inside said nozzle, forms a straight pipe having an inner diameter larger than the diameter of said optical fiber and less than 0.5 mm.

13. An apparatus for fabricating a coated optical fiber as claimed in claim 12, characterized in that said first layer and/or second layer coating materials are extruded into a gap defined between said nipple and said die, so that said optical fiber is coated with said coating materials in said nozzle of said die.

14. An apparatus for fabricating a coated optical fiber as claimed in claim 12, characterized in that the interior of said first cooling means is filled with coolant which is brought into contact with said coated optical fiber to cool said coated optical fiber.

15. An apparatus for fabricating a coated optical fiber as claimed in claim 14, characterizing by further comprising second means for cooling said coolant which is to be introduced into the interior of said first cooling means, and means for circulating said coolant between said first cooling means and said second cooling means.

Patentansprüche

1. Beschichtete optische Faser mit einer optischen Faser, einer ersten Schicht, die eine Kautschukmischung ist und um den Umfang der erwähnten optischen Faser herum angeordnet ist, und einer zweiten Schicht, die eine thermoplastische Harzmischung ist und um den Umfang der erwähnten ersten Schicht herum angeordnet ist, dadurch gekennzeichnet, daß (a) die erwähnte Kautschukmischung der erwähnten ersten Schicht eine thermoplastische Kautschukmischung ist, die einen Elastizitätsmodul von 0,1 GPa oder weniger hat und durch Extrusion auftragbar ist, (b) die erwähnte thermoplastische Harzmischung der erwähnten zweiten Schicht in geschmolzenem Zustand die Fähigkeit zur Bildung eines Flüssigkristalls zeigt und ihr Orientierungszustand durch Zwangskühlung unmittelbar nach dem Beschichtungsschritt beibehalten wird und (c) die erwähnte thermoplastische Harzmischung einen linearen Ausdehnungskoeffizienten von  $7 \times 10^{-6} \text{ C}^{-1}$  oder weniger und einen Elastizitätsmodul von 4,3 GPa oder mehr hat und durch Extrusion auftragbar ist.

2. Beschichtete optische Faser nach Anspruch 1, dadurch gekennzeichnet, daß die thermoplastische Kautschukmischung der erwähnten ersten Schicht ein Styrol-Copolymer oder ein Olefin-Copolymer enthält.

3. Beschichtete optische Faser nach Anspruch 1, dadurch gekennzeichnet, daß die thermoplastische Harzmischung der erwähnten zweiten Schicht aus Polyethylenterephthalat-p-Hydroxybenzoësäure-Copolymer, das 40 bis 70 Mol-% p-Hydroxybenzoësäure enthält, oder aus einer Mischung, die aus dem erwähnten Copolymer und anderem Polymer hergestellt ist, besteht und daß die erwähnte Harzmischung bei einer Schergeschwindigkeit von  $10^2 \text{ s}^{-1}$  oder mehr molekulare Orientierung in Längsrichtung der Faser zeigt.

4. Beschichtete optische Faser nach Anspruch 1, dadurch gekennzeichnet, daß die thermoplastische Kautschukmischung der erwähnten ersten Schicht als Hauptbestandteile

25 A: ein Styrol/Butadien-Blockcopolymer (Styrolkonzentration: 20 bis 40 Masse-%),  
B: ein naphthenisches Weichmacheröl und  
C: ein Wärmestabilisierungsmittel

enthält und daß die Konzentrationen der einzelnen Bestandteile der erwähnten Mischung so festgelegt sind, daß

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$$\frac{B}{A + B} = 5 \text{ bis } 40 \text{ Masse-\% und } \frac{B}{A + B + C} = 2 \text{ Masse-\%}.$$

35 5. Beschichtete optische Faser nach Anspruch 1, dadurch gekennzeichnet, daß die erwähnte thermoplastische Harzmischung der erwähnten zweiten Schicht aus der Gruppe ausgewählt ist, die aus vollständig aromatischen Polyester, aromatisch-aliphatischen Polyester, vollständig aromatischen Polyesteramiden, aromatisch-aliphatischen Polyesteramiden, aromatischen Polyazomethinen, aromatischen Polyestercarbonaten, den Mischungen davon oder Mischungen der erwähnten hochmolekularen Substanzen mit den anderen hochmolekularen Substanzen besteht.

40 6. Verfahren zur Herstellung einer beschichteten optischen Faser, bei dem ein Vorformling für eine optische Faser versponnen wird, indem erhitzt wird, so daß der erwähnte Vorformling für eine optische Faser unter Bildung einer optischen Faser erweicht wird, dadurch gekennzeichnet, daß die erwähnte optische Faser durch Extrusion gleichzeitig mit (a) einer ersten Schicht aus einer thermoplastischen Kautschukmischung, die einen Elastizitätsmodul von 0,1 GPa oder weniger hat und durch Extrusion auftragbar ist, und (b) einer zweiten Schicht aus einer molekular orientierten thermoplastischen Harzmischung, die in geschmolzenem Zustand die Fähigkeit zur Bildung eines Flüssigkristalls zeigt und die einen linearen Ausdehnungskoeffizienten von  $7 \times 10^{-6} \text{ C}^{-1}$  oder weniger und einen Elastizitätsmodul von 4,3 GPa oder mehr hat und durch Extrusion auftragbar ist, beschichtet wird, wobei die erwähnte Beschichtung durch Extrusion unmittelbar nach dem Schritt des Verspinnens mit einem Auftragegerät durchgeführt wird, und daß von der erwähnten ersten und zweiten Schicht, die gleichzeitig aufgetragen werden, mindestens die erwähnte zweite Schicht auf die Kristallisationstemperatur der molekular orientierten thermoplastischen Harzmischung oder eine niedrigere Temperatur zwangsgekühlt wird, bevor die beschichtete optische Faser einen Abstand x vom Auslaß des Auftragegeräts erreicht, wobei  $x/V \leq 1$  und V (m/s) die Laufgeschwindigkeit der optischen Faser ist.

45 7. Verfahren zur Herstellung einer beschichteten optischen Faser nach Anspruch 6, dadurch gekennzeichnet, daß die erwähnte beschichtete optische Faser unter Verwendung eines Kühlmittels das aus der Gruppe aufgewählt ist, die aus Flüssigkeiten, Gasen oder den Mischungen davon, die eine spezifische Wärme von 0,1 kcal/kg.°C oder mehr bei einer gewöhnlichen Temperatur und eine

50 8. Wärmeleitfähigkeit von 0,01 kcal/m.h.°C oder mehr haben, besteht, zwangsgekühlt wird.

55 9. Verfahren zur Herstellung einer beschichteten optischen Faser nach Anspruch 6, dadurch gekennzeichnet, daß die erwähnte molekular orientierte thermoplastische Harzmischung eine thermotrope, flüssigkristallinische, hochmolekulare Substanz ist.

60 10. Verfahren zur Herstellung einer beschichteten optischen Faser nach Anspruch 6, dadurch gekennzeichnet, daß die erwähnte molekular orientierte thermoplastische Harzmischung aus Polyethylen-

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terephthalat-p-Hydroxybenzoësäure-Copolymeren, die 40 bis 70 Mol-% p-Hydroxybenzoësäure enthalten, oder aus Mischungen, die aus den erwähnten Copolymeren und anderen Polymeren hergestellt sind, ausgewählt ist und daß die erwähnte Harzmischung bei einer Schergeschwindigkeit von  $10^2 \text{ s}^{-1}$  oder mehr molekulare Orientierung in Längsrichtung der Faser zeigt.

- 6 10. Verfahren zur Herstellung einer beschichteten optischen Faser nach Anspruch 6, dadurch gekennzeichnet, daß die erwähnte thermoplastische Kautschukmischung ein Styrol-Copolymer oder ein Ethylen-*o*-Olefin-Copolymer enthält.
11. Verfahren zur Herstellung einer beschichteten optischen Faser nach Anspruch 6, dadurch gekennzeichnet, daß die erwähnte thermoplastische Kautschukmischung als Hauptbestandteile ein Styrol/Butadien-Blockcopolymer, das 20 bis 40 Masse-% Styrol enthält, ein naphthenisches Welchmacheröl und ein Wärmestabilisierungsmittel enthält und daß die Menge des erwähnten naphthenischen Welchmacheröls 5 bis 150 Masseteile je 100 Masseteile des erwähnten Styrol/Butadien-Blockcopolymer beträgt.
12. Verfahren zur Herstellung einer beschichteten optischen Faser, bei der unmittelbar nach dem Erspinnen einer optischen Faser aus einem Vorformling für eine optische Faser durch Erhitzen zum Erweichen des erwähnten Vorformlings für eine optische Faser die erwähnte optische Faser mit einer ersten Schicht aus einer thermoplastischen Kautschukmischung, die einen Elastizitätsmodul von 0,1 GPa oder weniger hat und durch Extrusion auftragbar ist, und einer zweiten Schicht aus einer molekular orientierten thermoplastischen Harzmischung, die in geschmolzenem Zustand die Fähigkeit zur Bildung eines Flüssigkristalls zeigt und die einen linearen Ausdehnungskoeffizienten von  $7 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$  oder weniger und einen Elastizitätsmodul von 4,3 GPa oder mehr hat und durch Extrusion auftragbar ist, beschichtet wird, dadurch gekennzeichnet, daß die erwähnte Vorrichtung einen Extruder zum Extrudieren der erwähnten thermoplastischen Kautschukmischung und der erwähnten molekular orientierten thermoplastischen Harzmischung, einen Querkopf zum gleichzeitigen Beschichten der erwähnten optischen Faser mit der extrudierten thermoplastischen Kautschukmischung und der extrudierten molekular orientierten thermoplastischen Harzmischung, wodurch um die erwähnte optische Faser herum die erwähnte erste Schicht und die erwähnte zweite Schicht gebildet werden, und eine erste Kühleinrichtung mit einer Länge  $x$  (m), die für eine mit einer Geschwindigkeit  $V$  (m/s) laufende Faser die Bedingung  $x/V \leq 1$  erfüllt, aufweist, wobei die erste Kühleinrichtung zur Zwangskühlung der beschichteten optischen Faser bei einer Flüssigkristall-Übergangstemperatur der flüssigkristallinischen thermoplastischen Harzmischung der zweiten Schicht oder einer niedrigeren Temperatur an der Auslaßseite des erwähnten Querkopfes angeordnet ist, und daß der erwähnte Querkopf mindestens einen Nippel-Preßform-Satz aufweist und ein innerhalb der Düse der erwähnten Preßform befindlicher Endteil des erwähnten Nippels ein gerades Rohr bildet, dessen Innendurchmesser größer als der Durchmesser der erwähnten optischen Faser und kleiner als 0,5 mm ist.
13. Vorrichtung zur Herstellung einer beschichteten optischen Faser nach Anspruch 12, dadurch gekennzeichnet, daß die Beschichtungsmaterialien für die erwähnte erste Schicht und/oder die erwähnte zweite Schicht in einem Zwischenraum extrudiert werden, der zwischen dem erwähnten Nippel und der erwähnten Preßform abgegrenzt ist, so daß die erwähnte optische Faser in der erwähnten Düse der erwähnten Preßform mit den erwähnten Beschichtungsmaterialien beschichtet wird.
14. Vorrichtung zur Herstellung einer beschichteten optischen Faser nach Anspruch 12, dadurch gekennzeichnet, daß der Innenraum der erwähnten ersten Kühleinrichtung mit Kühlmittel gefüllt ist, das mit der erwähnten beschichteten optischen Faser in Berührung gebracht wird, um die erwähnte beschichtete optische Faser zu kühlen.
15. Vorrichtung zur Herstellung einer beschichteten optischen Faser nach Anspruch 14, dadurch gekennzeichnet, daß es ferner eine zweite Kühleinrichtung für die Kühlung des erwähnten Kühlmittels, das in den Innenraum der erwähnten ersten Kühleinrichtung eingeführt werden soll, und eine Einrichtung zum Umlaufenlassen des erwähnten Kühlmittels zwischen der erwähnten ersten Kühleinrichtung und der erwähnten zweiten Kühleinrichtung aufweist.

### 50 Revendications

1. Une fibre optique enduite comprenant une fibre optique, une première couche qui consiste en une composition de caoutchouc et qui est placée autour de la fibre optique, et une seconde couche qui est une composition de résine thermoplastique et qui est placée autour de la première couche, caractérisée en ce que (a) la composition de caoutchouc de la première couche est une composition de caoutchouc thermoplastique qui a un module d'Young de 0,1 GPa ou moins et qu'on peut utiliser dans une opération d'enduction par extrusion, (b) la composition de résine thermoplastique de la seconde couche présente la propriété de former des cristaux liquides dans l'état fondu, et son état orienté est maintenu par un refroidissement forcé immédiatement après l'étape d'enduction, et (c) la composition de résine thermoplastique à un coefficient de dilatation linéaire de  $7 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$  ou moins, et un module d'Young de 4,3 GPa ou plus, et on peut l'utiliser dans une opération d'enduction par extrusion.
2. Une fibre optique enduite selon la revendication 1, caractérisée en ce que la composition de caoutchouc thermoplastique de la première couche contient un copolymère de styrène ou un copolymère d'oléfine.

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3. Une fibre optique enduite selon la revendication 1, caractérisée en ce que la composition de résine thermoplastique de la seconde couche consiste en un copolymère de téraphthalate de polyéthylène-acide parahydroxybenzoïque, contenant un pourcentage molaire de 40 à 70% d'acide parahydroxybenzoïque, ou bien elle consiste en un mélange préparé à partir de ce copolymère et d'un autre polymère, et cette composition de résine présente une orientation moléculaire dans la direction longitudinale de la fibre, à une vitesse de cisaillement de  $10^2 \text{ s}^{-1}$  ou plus.

4. Une fibre optique enduite selon la revendication 1, caractérisée en ce que la composition de caoutchouc thermoplastique de la première couche comprend, pour ses principaux composants:

A: un copolymère bloc de styrène/butadiène (avec une concentration de 20—40% en poids de styrène),  
B: une huile plastifiante naphténique, et  
C: un stabilisant thermique,  
et en ce que les concentrations des composants respectifs de la composition sont déterminées de façon à avoir

$$\frac{B}{A + B} = 5-40 \text{ et } \frac{B}{A + B + C} \geq 2\% \text{ en poids.}$$

5. Une fibre optique enduite selon la revendication 1, caractérisée en ce que la composition de résine thermoplastique de la seconde couche est sélectionnée dans le groupe comprenant tous les polyesters aromatiques, les polyesters aromatiques gras, toutes les amides de polyesters aromatiques, les amides de polyesters aromatiques-alphabétiques, les polyazométhines aromatiques, les carbonates de polyesters aromatiques, leurs mélanges, ou des mélanges de ces matières à poids moléculaire élevé avec d'autres matières à poids moléculaire élevé.

6. Un procédé de fabrication d'une fibre optique enduite, dans lequel on soumet une préforme de fibre optique à une opération de fibrage par chauffage, de façon que cette préforme de fibre optique se ramollisse pour former une fibre optique, caractérisé en ce qu'on enduit simultanément la fibre optique, par extrusion, avec (a) une première couche d'une composition de caoutchouc thermoplastique qui a un module d'Young de 0,1 GPa ou moins et qui peut faire l'objet d'une opération d'enduction par extrusion, et (b) une seconde couche d'une composition de résine thermoplastique présentant une orientation moléculaire, qui a la propriété de former des cristaux liquides dans un état fondu, et qui a un coefficient de dilatation linéaire de  $7 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$  ou moins qui a un module d'Young de 4,3 GPa ou plus et qui peut faire l'objet d'une opération d'enduction par extrusion; cette opération d'enduction par extrusion étant accomplie immédiatement après l'étape de fibrage, au moyen d'un applicateur, et en ce que la seconde couche, au moins, parmi les première et seconde couches formées simultanément, est soumise à un refroidissement forcé jusqu'à la température de cristallisation de la composition de résine thermoplastique à orientation moléculaire, ou jusqu'à une température inférieure, avant que la fibre optique enduite n'atteigne une distance  $x$  à partir de la sortie de l'aplicateur, avec  $x/V \leq 1$  et en désignant par  $V$  (m/s) la vitesse de déplacement de la fibre optique.

7. Un procédé de fabrication d'une fibre optique enduite selon la revendication 6, caractérisé en ce que la fibre optique enduite est soumise à un refroidissement forcé par l'utilisation d'un agent de refroidissement, qui est sélectionné dans le groupe comprenant des liquides et des gaz, ou des mélanges de ceux-ci, ayant une chaleur spécifique de 0,1 kcal/kg·°C ou plus à une température ordinaire, et une conductivité thermique de 0,01 kcal/m.h.°C ou plus.

8. Procédé de fabrication d'une fibre optique enduite selon la revendication 6, caractérisé en ce que la composition de résine thermoplastique à orientation moléculaire est une matière à poids moléculaire élevé l'état de cristaux liquides thermotropes.

9. Procédé de fabrication d'une fibre optique enduite selon la revendication 6, caractérisé en ce que la composition de résine thermoplastique à orientation moléculaire est sélectionnée parmi des copolymères de téraphthalate de polyéthylène-acide parahydroxybenzoïque contenant un pourcentage molaire de 40—70% d'acide parahydroxybenzoïque, ou des mélanges préparés à partir de ces copolymères et d'autres polymères, et en ce que la composition de résine présente une orientation moléculaire, dans la direction longitudinale de la fibre, à une vitesse de cisaillement de  $10^2 \text{ s}^{-1}$  ou plus.

10. Un procédé de fabrication d'une fibre optique enduite selon la revendication 6, caractérisé en ce que la composition de caoutchouc thermoplastique contient un copolymère de styrène ou un copolymère d'éthylène- $\alpha$ -oléfine.

11. Un procédé de fabrication d'une fibre optique enduite selon la revendication 6, caractérisé en ce que la composition de caoutchouc thermoplastique comprend un copolymère bloc de styrène/butadiène contenant 20 à 40% en poids de styrène, une huile plastifiante naphténique et un stabilisant thermique, en tant que principaux constituants, et en ce que la proportion d'huile plastifiante naphténique est de 5—150 parties en poids pour 100 parties en poids du copolymère bloc de styrène-butadiène.

12. Un appareil pour fabriquer une fibre optique enduite dans lequel, immédiatement après la fabrication d'une fibre optique par fibrage à partir d'une préforme de fibre optique, par chauffage de façon à ramollir la préforme de fibre optique, cette fibre optique est enduite avec une première couche d'une composition de caoutchouc thermoplastique qui a un module d'Young de 0,1 GPa ou moins et qui peut

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faire l'objet d'une opération d'enduction par extrusion, et avec une seconde couche d'une composition de résine thermoplastique à orientation moléculaire qui présente la propriété de former des cristaux liquides dans un état fondu et qui a un coefficient de dilatation linéaire de  $7 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  ou moins et un modulé d'Young de 4,3 GPa ou plus, et qui peut faire l'objet d'une opération d'enduction par extrusion, caractérisé

5 en ce que cet appareil comprend une machine d'extrusion pour extruder la composition de caoutchouc thermoplastique et la composition de résine thermoplastique à orientation moléculaire, une tête d'équerre pour enduire simultanément la fibre optique avec la composition de caoutchouc thermoplastique extrudée et la composition de résine thermoplastique à orientation moléculaire extrudée, pour former les première et seconde couches autour de la fibre optique, et des premiers moyens de refroidissement, ayant une  
10 longueur  $x$  (m) qui satisfait la condition  $x/V \leq 1$  pour une fibre qui se déplace à une vitesse  $V$  (m/s), qui sont disposés du côté de la sortie de la tête d'équerre, pour soumettre la fibre optique enduite à un refroidissement forcé jusqu'à une température de transition de cristaux liquides de la composition de résine thermoplastique à structure de cristaux liquides de la seconde couche, ou jusqu'à une température inférieure, et en ce que la tête d'équerre comporte au moins un ensemble formé par une buse et une filière,  
15 et une partie d'extrémité distale de la buse, qui se trouve à l'intérieur du passage de la filière, forme un tube rectiligne ayant un diamètre intérieur supérieur au diamètre de la fibre optique et inférieur à 0,5 mm.

13. Un appareil pour fabriquer une fibre optique enduite selon la revendication 12, caractérisé en ce que les matières d'enduction de la première couche et/ou de la seconde couche sont extrudées dans un espace qui est défini entre la buse et la filière, de façon qui la fibre optique soit enduite avec les matières  
20 d'enduction dans le passage de la filière.

14. Un appareil pour fabriquer une fibre optique enduite selon la revendication 12, caractérisé en ce que l'intérieur des premiers moyens de refroidissement est rempli d'un agent de refroidissement qui est amené en contact avec la fibre optique enduite, pour la refroidir.

15. Un appareil pour fabriquer une fibre optique enduite selon la revendication 14, caractérisé en ce que  
25 qu'il comprend en outre des seconds moyens pour refroidir l'agent de refroidissement qui est introduit à l'intérieur des premiers moyens de refroidissement, et des moyens pour faire circuler cet agent de refroidissement entre les premiers moyens de refroidissement et les seconds moyens de refroidissement.

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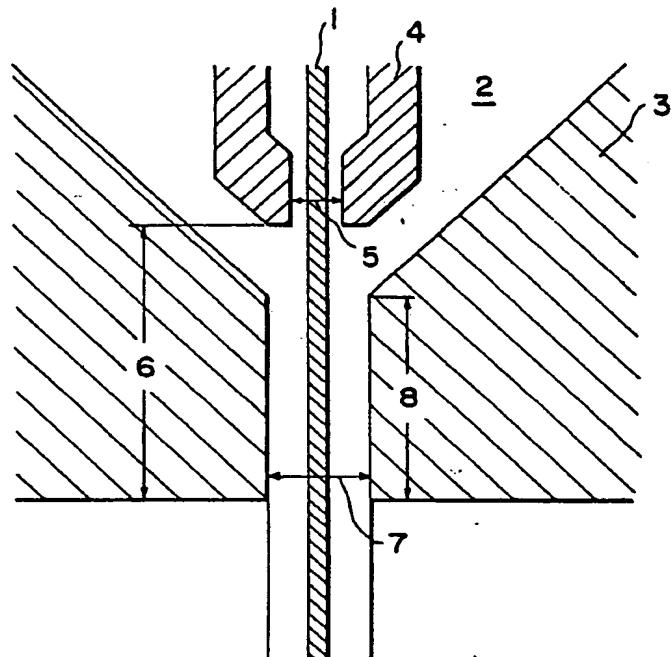
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PRIOR ART



*FIG. I*

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PRIOR ART

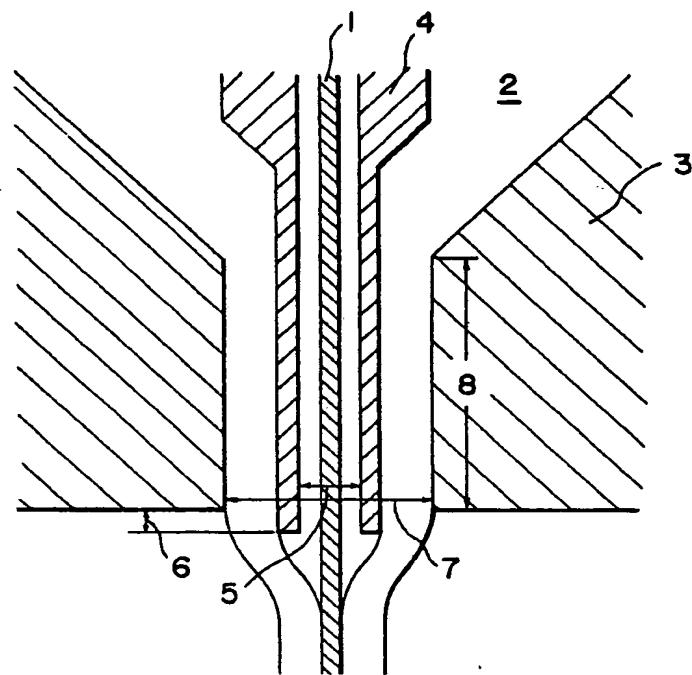


FIG. 2

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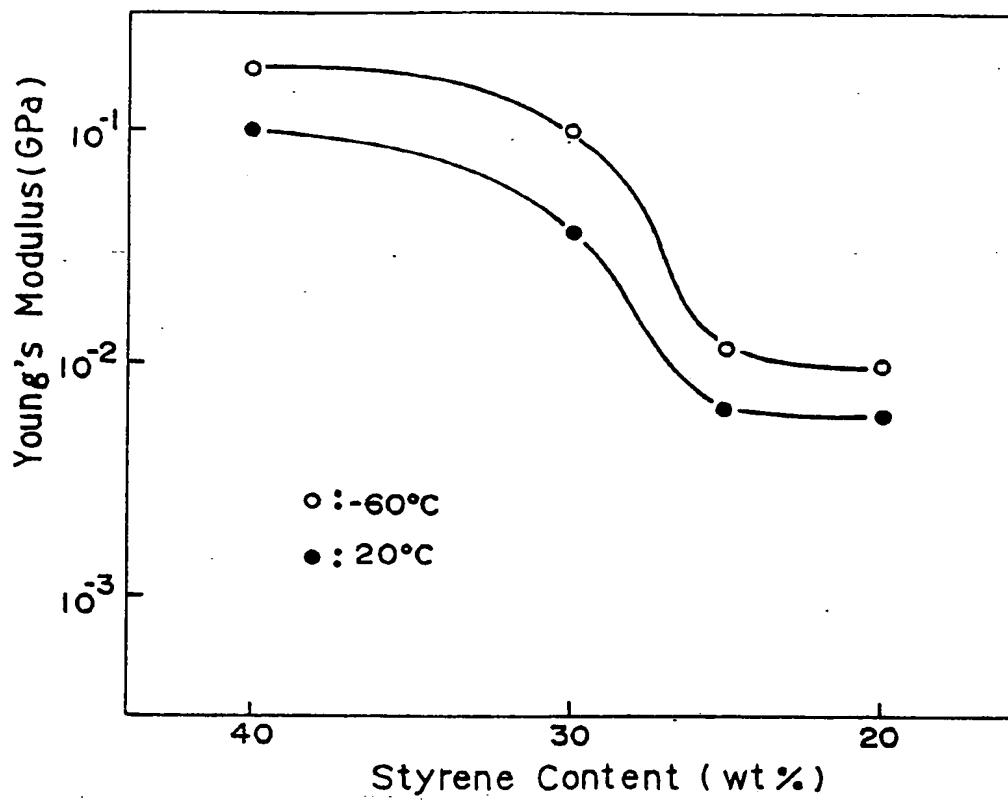
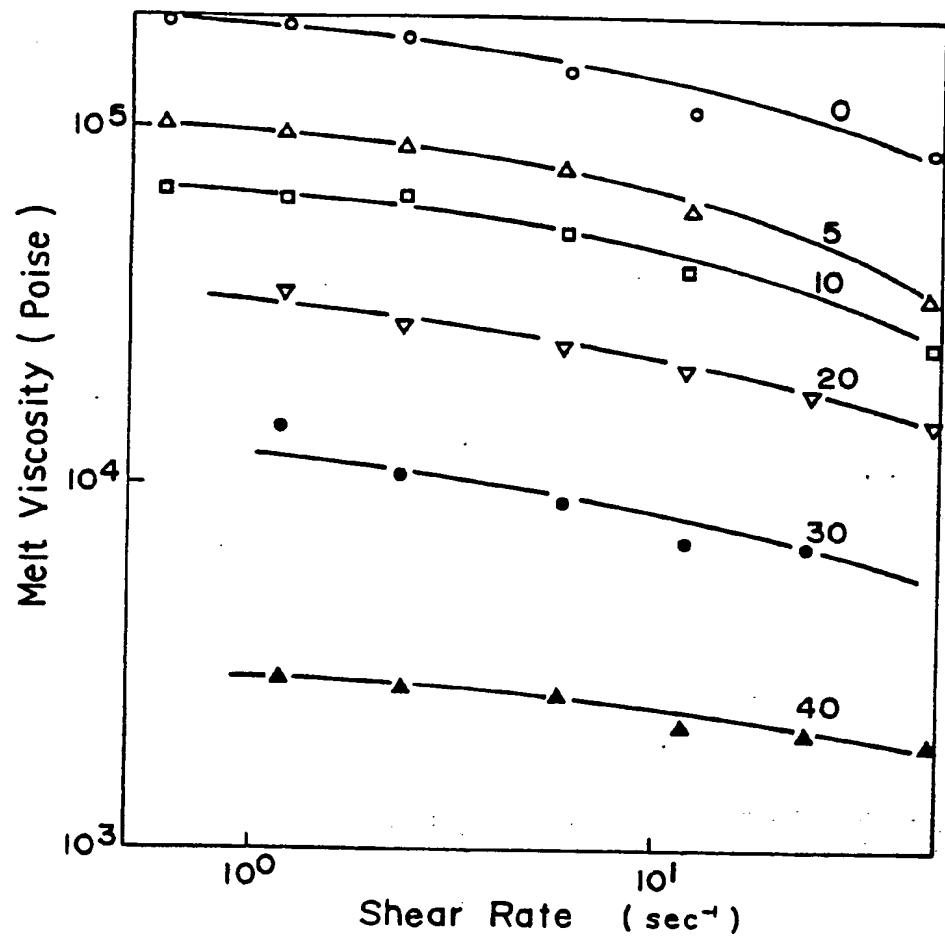


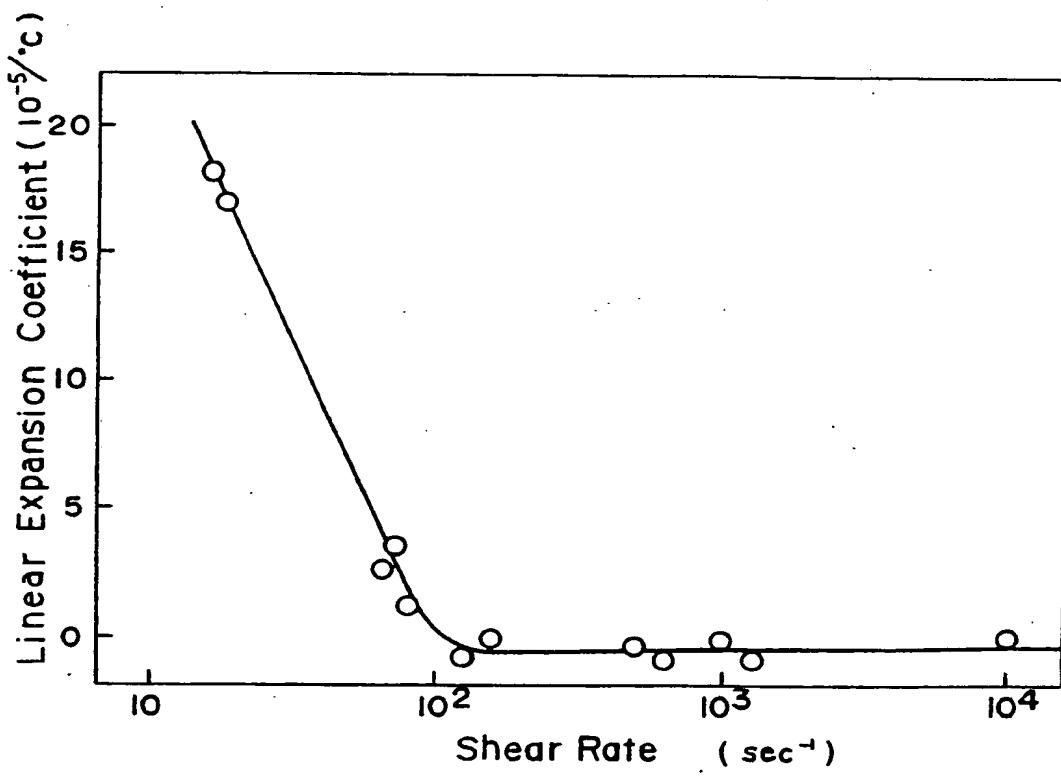
FIG.3

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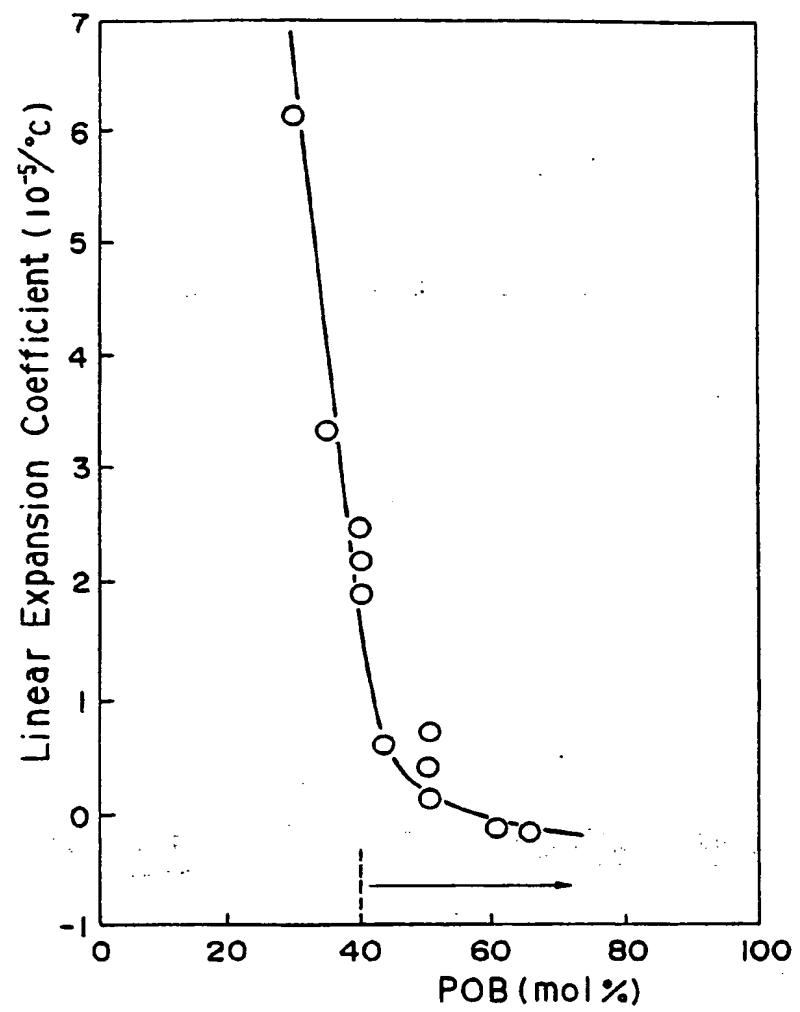
**FIG.4**

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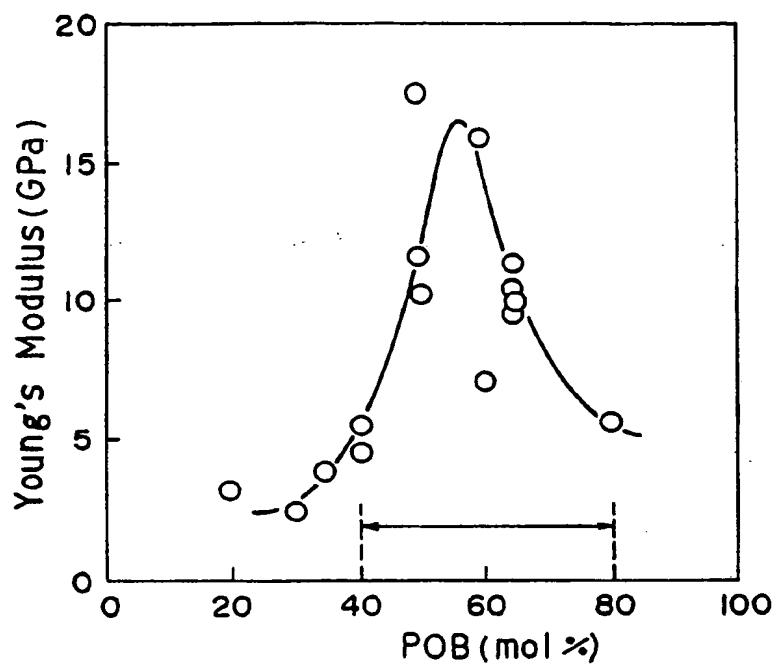
**FIG.5**

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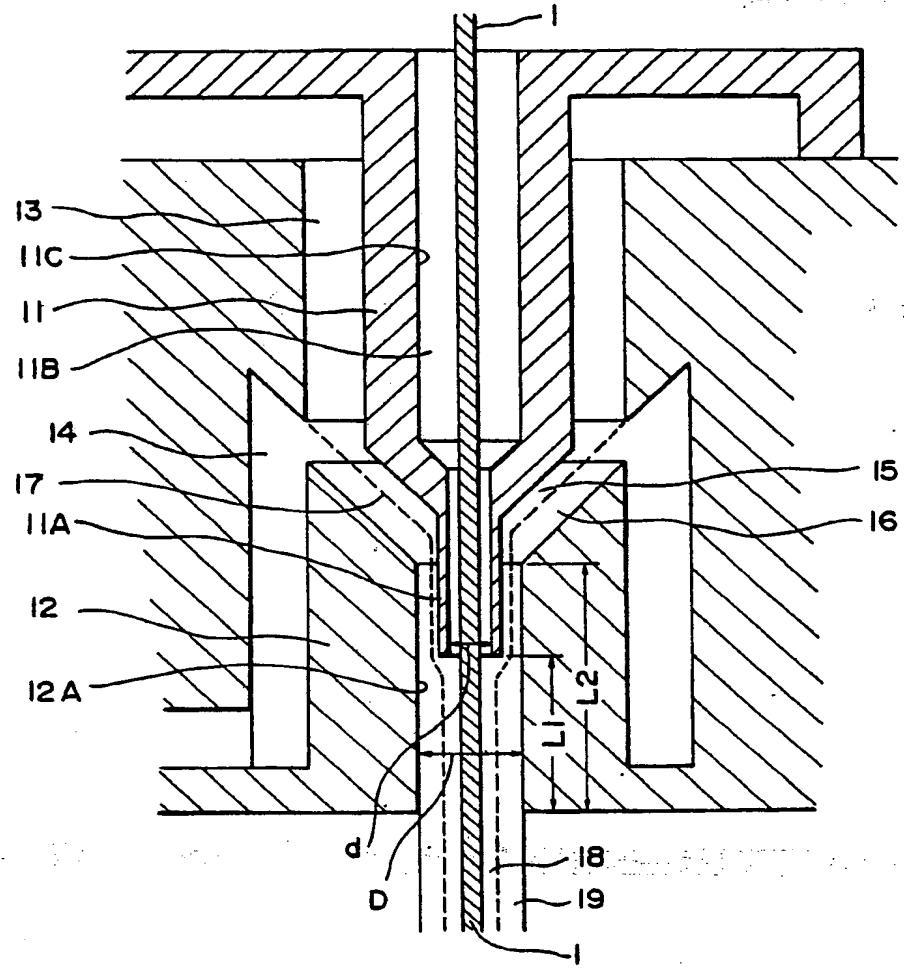
**FIG.6A**

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**FIG.6B**

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**FIG. 7**

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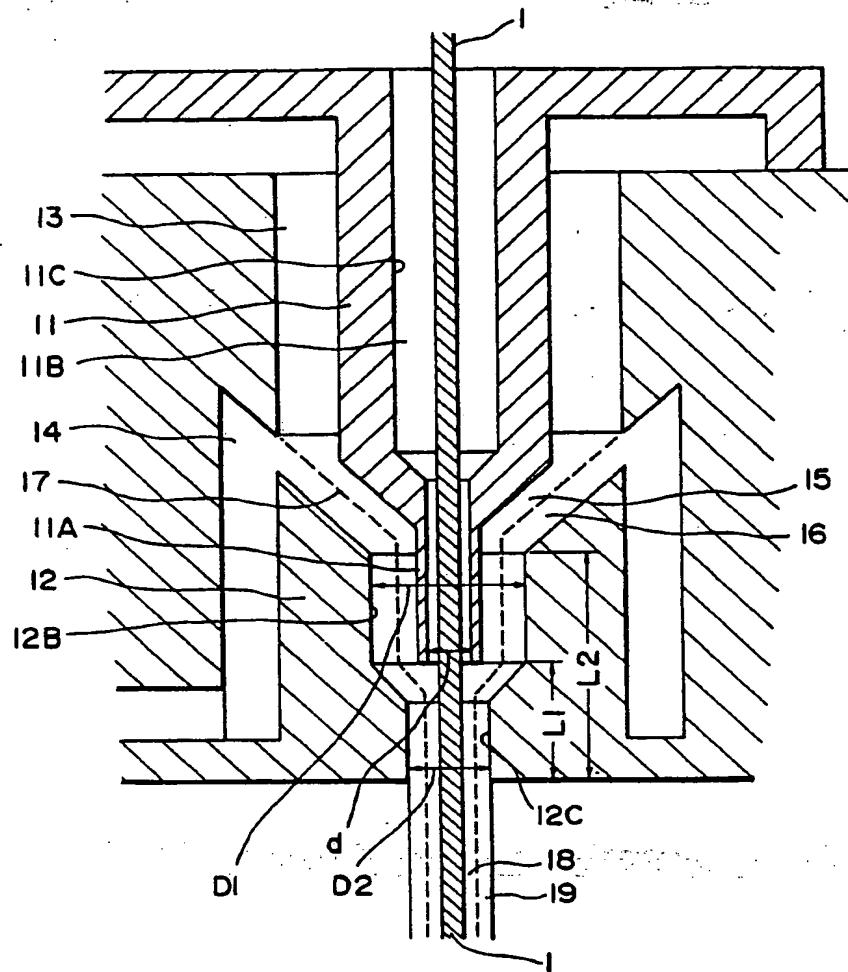


FIG. 8

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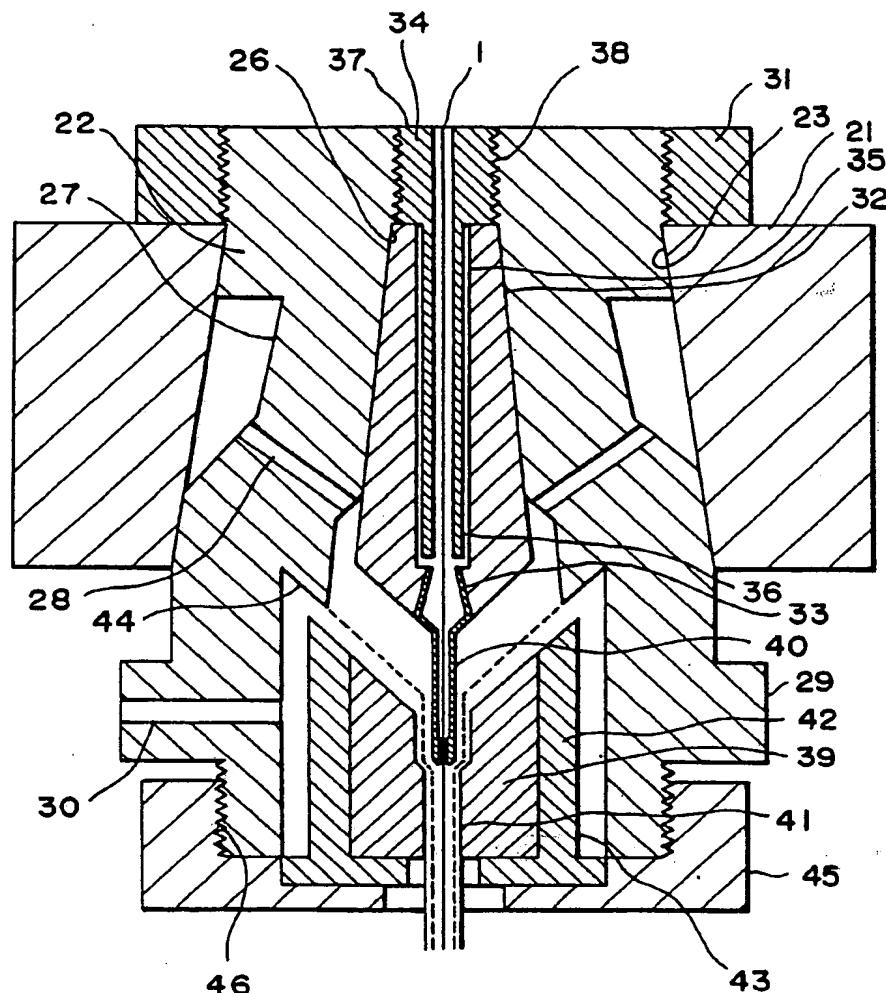


FIG. 9

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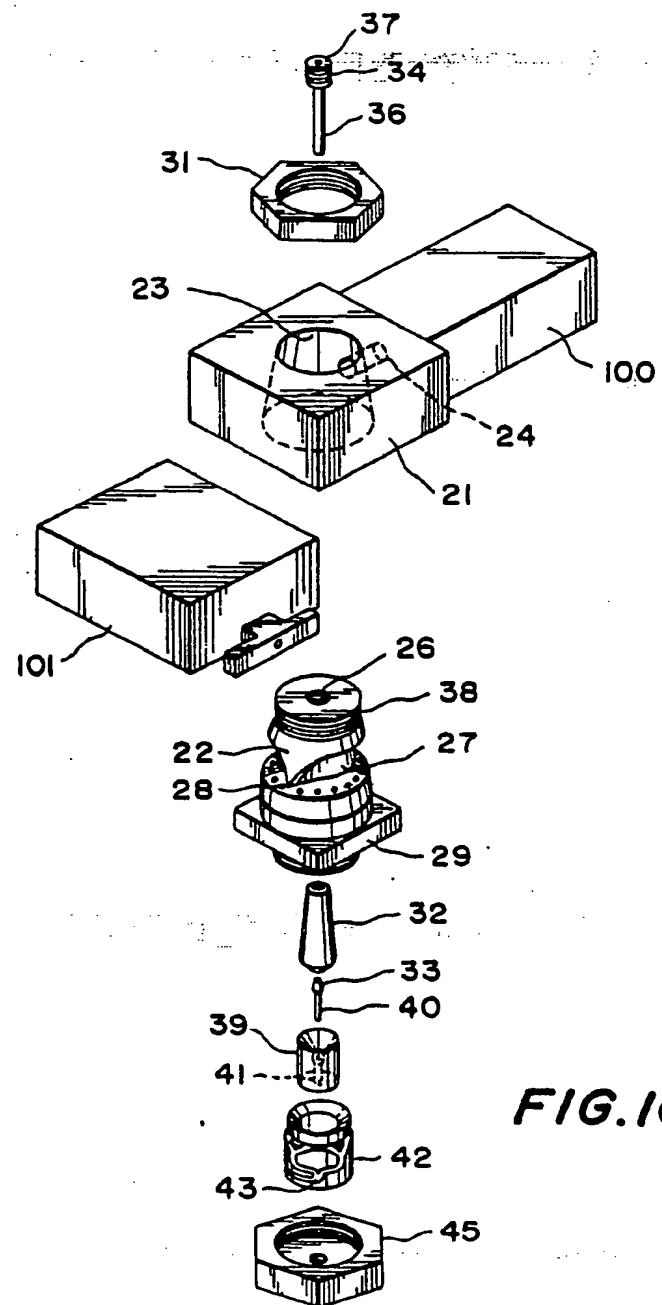


FIG. 10

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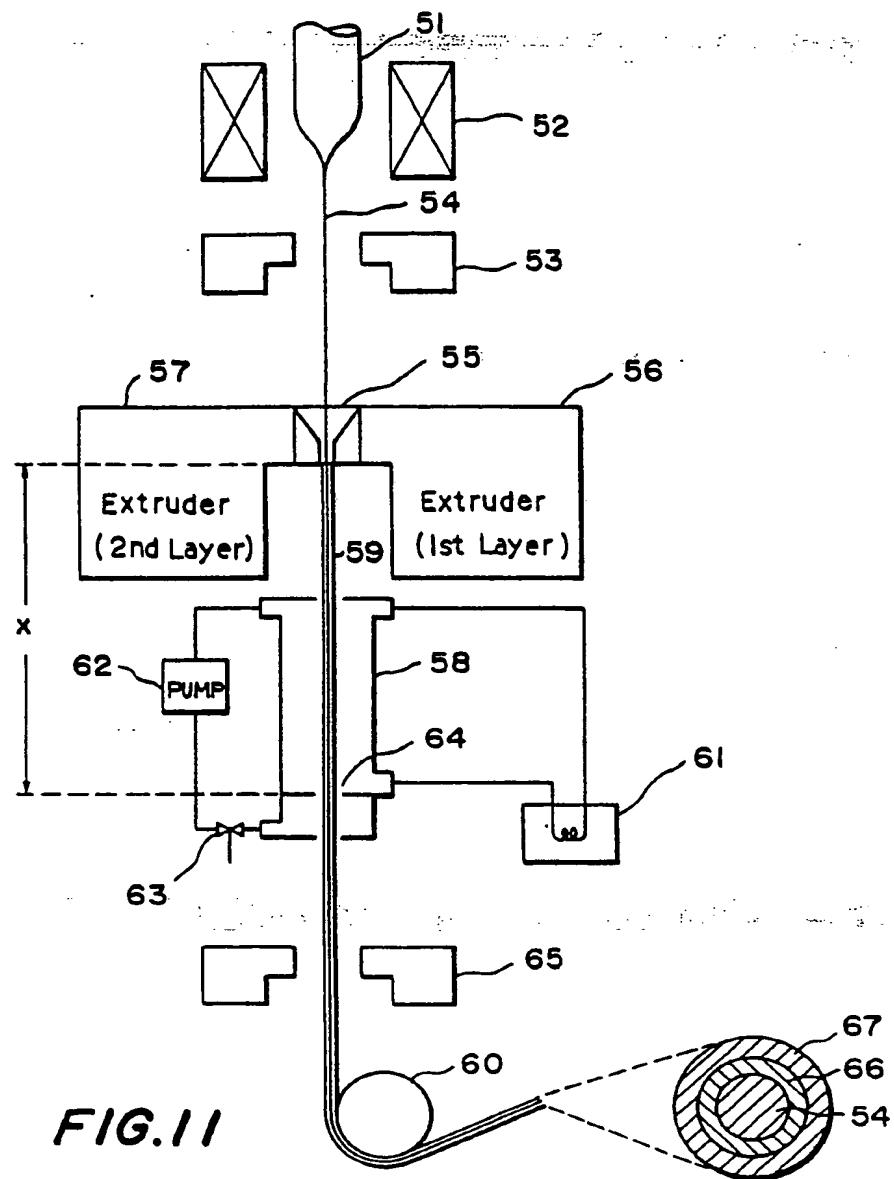
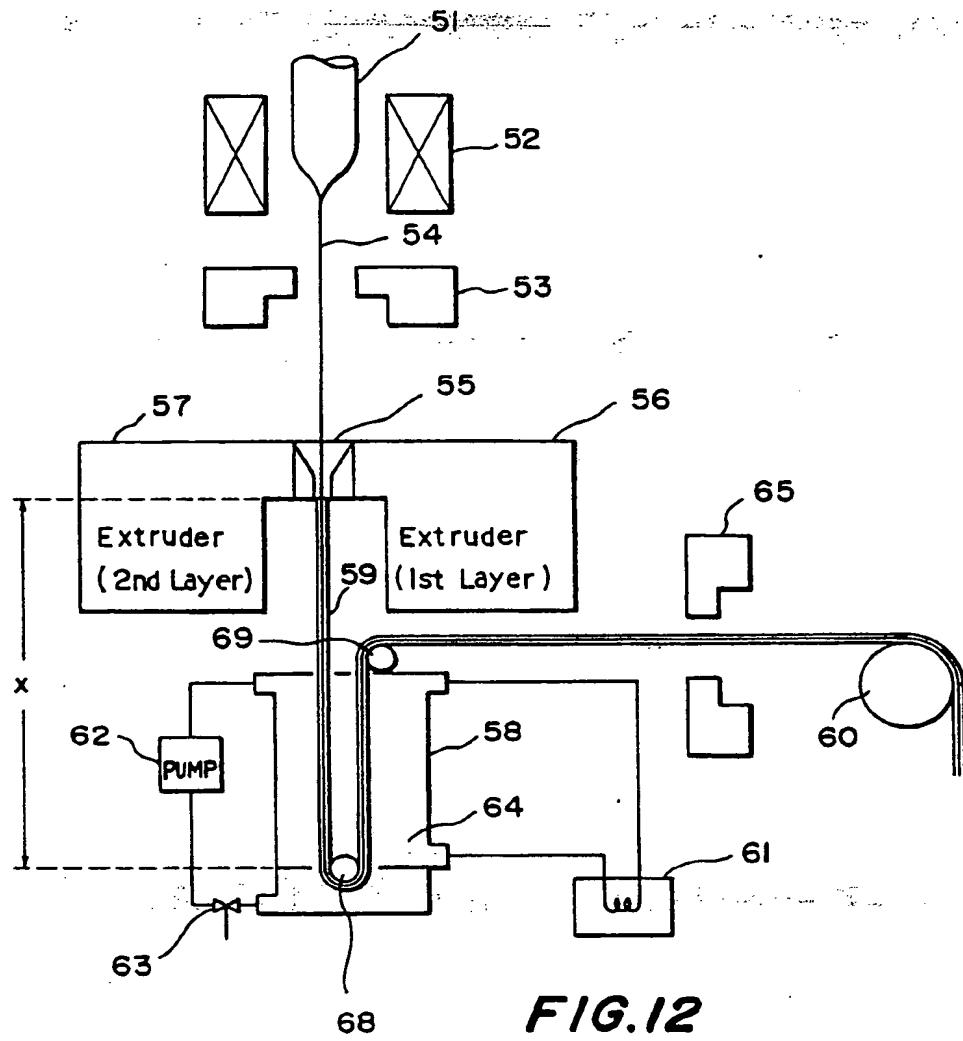


FIG.11

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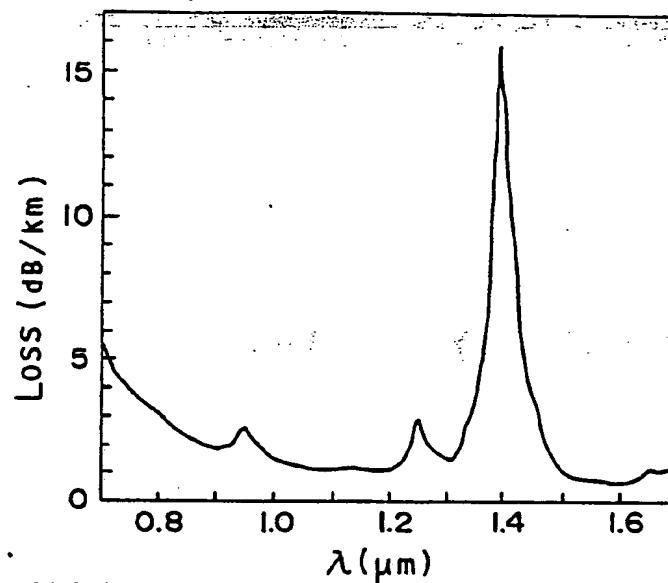


FIG.13

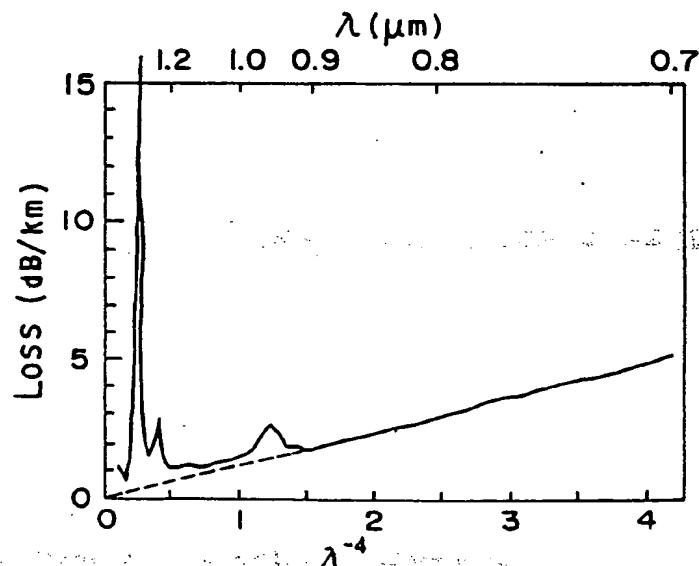


FIG.14

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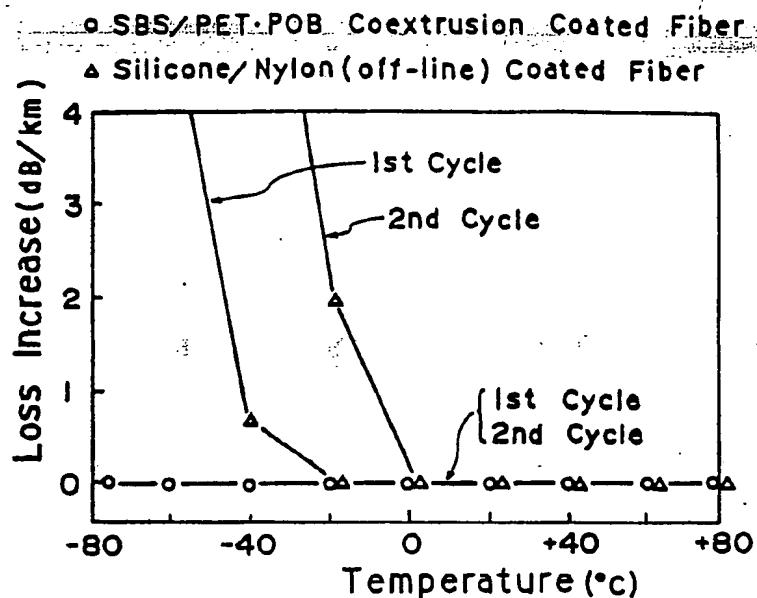


FIG.15

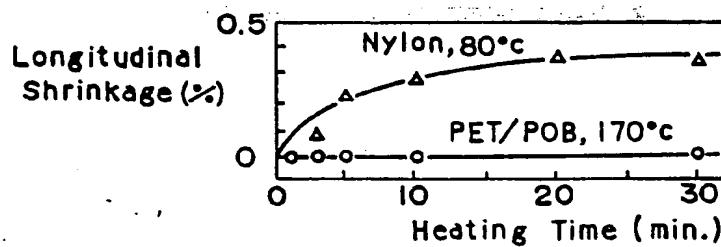


FIG.16



European Patent  
Office

EUROPEAN SEARCH REPORT

0155070

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85300402.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	<p>PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 6, no. 31, February 24, 1982</p> <p>THE PATENT OFFICE JAPANESE GOVERNMENT</p> <p>page 61 C 92</p> <p>* Kokai-no. 56-149 353 (NIPPON DENSHIN DENWA KOSHA) *</p> <p>--</p>	1,11, 19	C 03 C 25/02 G 02 B 6/22
A	<p><u>DE - A1 - 3 147 137 (SIEMENS AG)</u></p> <p>* Claims 1,5-7; page 3, line 28 - page 4, line 3 *</p> <p>--</p>	1,5	
A	<p>PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 6, no. 118, July 2, 1982</p> <p>THE PATENT OFFICE JAPANESE GOVERNMENT</p> <p>page 153 C 111</p> <p>* Kokai-no. 57-47 748 (NIPPON DENSHIN DENWA KOSHA) *</p> <p>----</p>	1,5	<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 4)</p> <p>C 03 C G 02 B</p>
<p>The present search report has been drawn up for all claims</p>			
Place of search VIENNA	Date of completion of the search 30-04-1985	Examiner HAUSWIRTH	
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p>			

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